Petrology and Geochemistry of the Carbonates, Ballagan Formation, N.W. Midland Valley, Scotland

by

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Submitted for a Doctorate of Philosophy

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To my parents, my wife,

my children, my brothers

and my sisters.

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ABSTRACT

This study investigates the nodular and stratified carbonate beds in the Ballagan Formation, in the Western Midland Valley of Scotland. The Ballagan Formation, which also includes lutites and quartz arenites, lies stratigraphically between the Upper Old Red Sandstone and the Spout of Ballagan Sandstone: it constitutes the lower-most part of the Calciferous Sandstone Measures.

Microscopic examination of thin sections showed that the carbonates comprise mainly three microfacies which are subdivided on the basis of fabric and crystal-size. Microfacies A is the finest-grained and from it the other two have diagenetically evolved, through neomorphism (Microfacies B), and metasomatism and segregation (Microfacies C). Microfacies B has resulted from multiple neomorphic stages as indicated by crystal-size variation. As a result of neomorphism, clay has concentrated in the inter-crystalline boundaries, leaving the new crystals slightly clearer than their precursors. Microfacies C has developed in two ways: (1) metasomatism and (2) segregation. Calcitization of dolomitic beds and segregation of calcite in an original argillaceous sediment, both produced Microfacies C. The controlling factors over these processes are unknown.

Shrinkage cracks, cavity-cement, and veinlets are common features in both stratified and nodular carbonates. Poorly preserved /

preserved laminations are uncommon in the untreated rock specimen, but are common in thin section. Whilst it is difficult to prove an algal origin for these structures, they morphologically resemble algal laminations.

Calculation of mineral proportions from chemical analyses by X-ray fluorescence show that c 86% of the carbonate beds contain more than 50% of the mineral dolomite, therefore, they are generally dolomites by definition, with minor limestone occurrences. Terrigeneous material content is composed mainly of clay minerals; illite, chlorite, and montmorillonite with common quartz. Gypsum is a minor lithology in the rock assemblages.

Electron microprobe analysis has shown that crystals of both Microfacies A and B are composed mainly of dolomite, the crystals of the first contain more clay than those of the latter. Crystals of Microfacies C are composed of calcite. Probing of veinlets confirmed a wide range of mineral compositions.

From a consideration of the fineness, bed-thickness, structures, faunas, composition, rock-association and lateral facies relationships, these beds are thought to have formed in a lagoonal environment. On the seaward the lagoon was probably bounded by sand bars; on the landward by caliche pavements and alluvium. The best analogous environment is seen in the Coorong, S. Australia, where fine dolomitic beds are laid down during the wet season and desiccated during the dry.

CHAPTER ONE

INTRODUCTION

1.1 The General Nature and Distribution of the Ballagan Formation

The Ballagan Formation known as the Ballagan Beds or the Cementstone Group, comprises a rapid alternation of carbonates (predominantly dolomites), lutites and sandstone. The outcrops of the strata in the west of the Midland Valley are shown in Figure 1.1. These strata constitute the lower-most part of the well known Calciferous Sandstone Measures of the lower Carboniferous system in Scotland (Figure 1.2).

In the study area, where the formation base is exposed, it is found underlain by rocks assigned to the Upper Old Red Sandstone. However, the contact between the two suites of rocks is transitional and usually concealed.

The formation is capped either by the Spout of Ballagan Sandstone (or its equivalent the Downie's Loup Sandstone), or the Clyde Plateau Lavas, the latter replacing it completely in some places. As with the base, the overlying sediments are not always present.

The succession is generally characterised by the frequent occurrence/

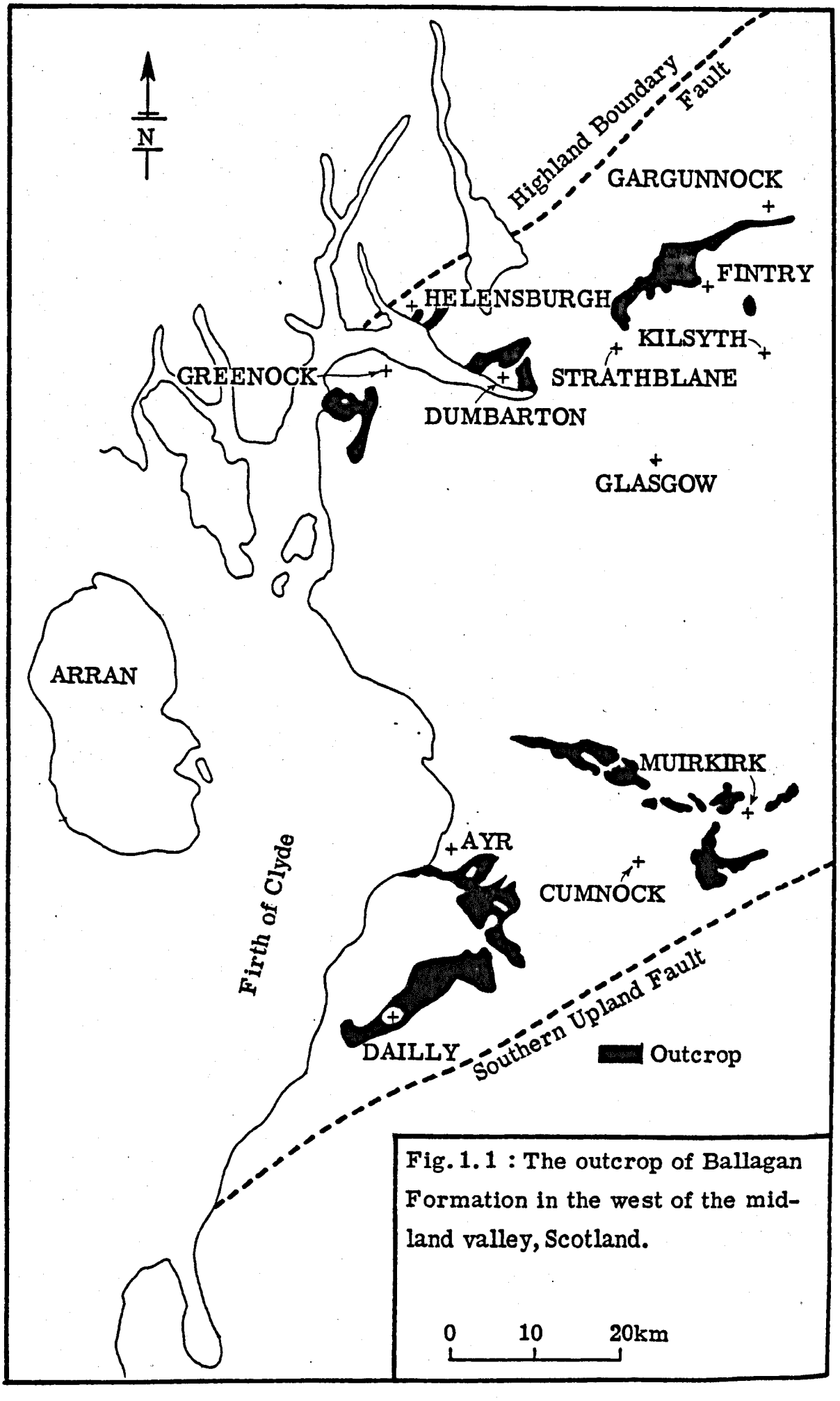

Fig. 1.1 : The outcrop of Ballagan Formation in the west of the mid-land valley, Scotland.

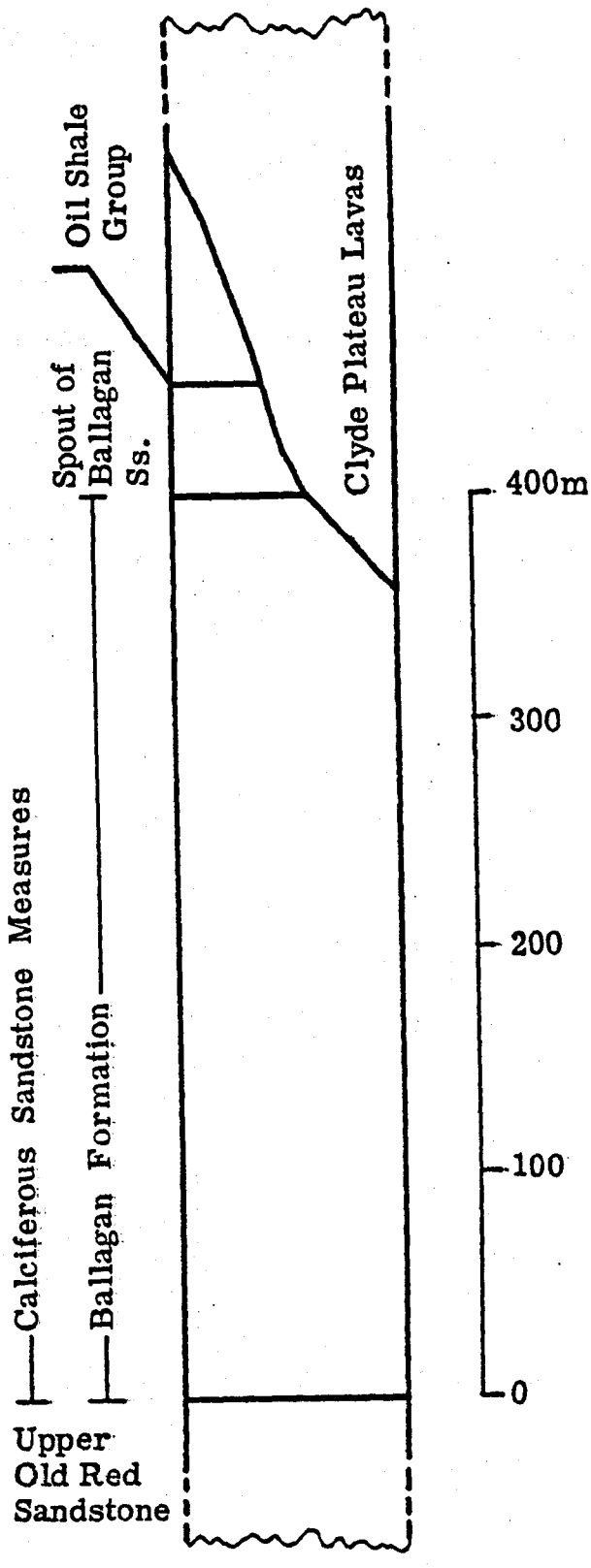

Fig. 1.2 : Section showing the position of the Ballagan Formation. The Clyde Plateau Lavas rest on Upper Old Red Sandstone in Ayrshire. (Ballagan Fm. thickness 400m taken from Stirling Sheet, Spout of Ballagan Sandstone thickness 30m taken from Francis, 1965).

occurrence of sandstone horizons towards the base, and their scarcity in the upper part, and by the wide range of lutites thickness at the lower part, compared with that of the upper part.

The lutites constitute the highest proportion of the succession in terms of both number of occurrences and thickness. They contain gypsum sheets filling vertical and diagonal joints and along bedding planes. The carbonates occur in nodular and stratified form, they are usually relatively very thin. They are generally cracked and contain secondary minerals, such as calcite; dolomite; gypsum; celestine; and baryte, in the form of veinlets and cavity-cement. Some layers are brecciated as they are found composed of concentrations of carbonates in an argillaceous matrix.

There is no section with complete exposure through the whole Ballagan Formation. However, parts of the sequence are very well exposed in some places.

1.2 Area of Investigation

The area included in the present study is located in the northwest of the Midland Valley of Scotland and lies between Glasgow: Stirling and Greenock (Figure 1.3). Several natural exposures in this area are involved in the investigation, where detailed logging is possible.

1.3/

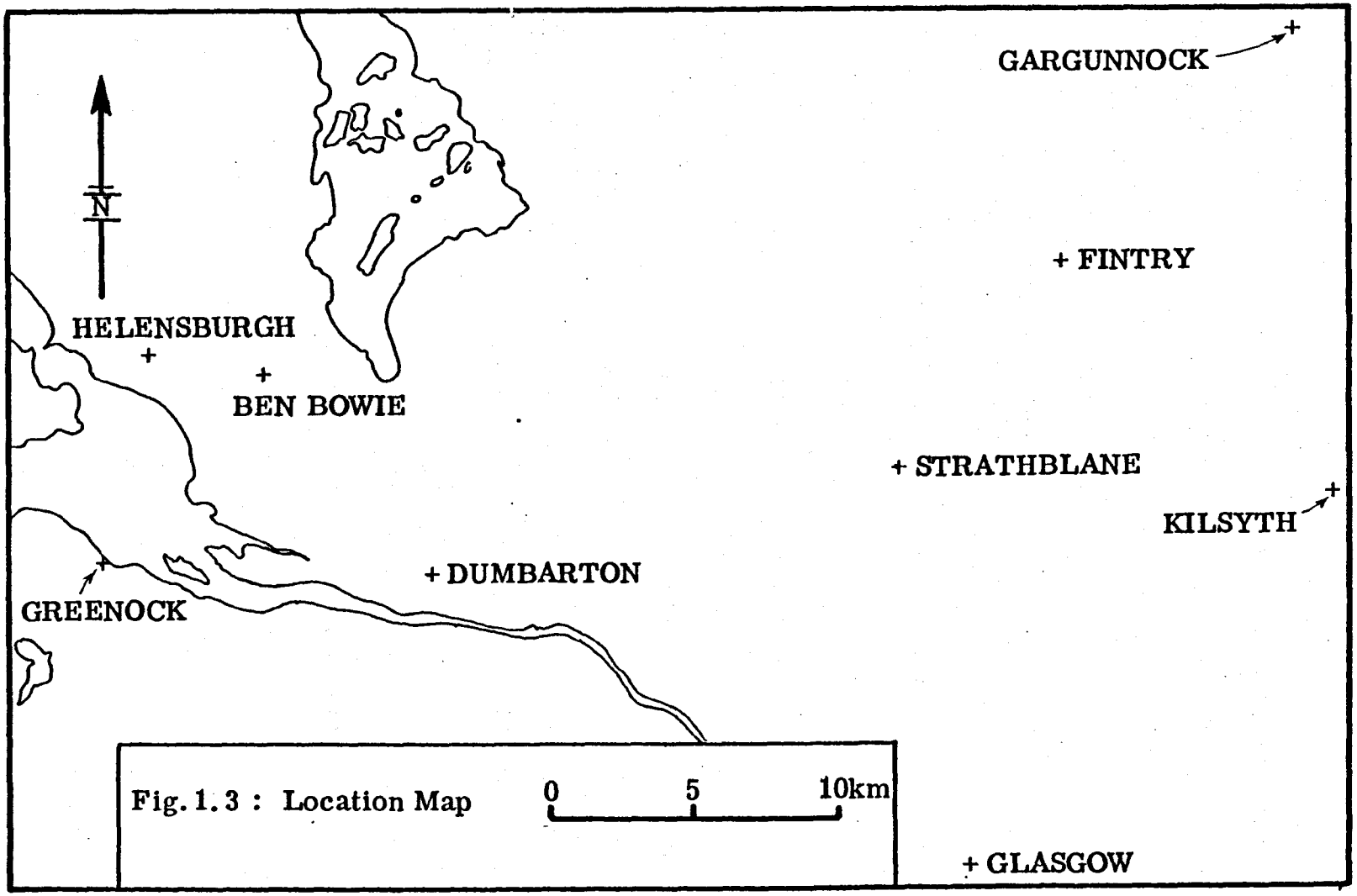

Fig. 1.3 : Location Map

1.3 History of Previous Work

The work on the Ballagan Beds deposits in the study area was begun around the middle of the nineteenth century. Young (1860) published his paper titled "Geology of the Campsie District" as the first edition of the Transactions of the Glasgow Geological Society. These deposits were described in Ballagan Glen, their type locality, as the finest section where a succession of inter-bedded limestone, sandstone and marly shale is seen capped by massive beds of white sandstone.

Young (1867) subsequently published the same paper in a revised form as a result of more work being carried out. The cementstones were described as nodular and layered, quite amorphous in structure and mainly grey in colour. Horizontal, white fibrous and nearly vertical, red gypsum layers were recorded. Chemical analyses showed that these cementstones contain between 23 and 27 per cent weight lime and between 14 and 17 per cent weight magnesia. It was suggested that the cementstones formed from the segregation of a dolomitic mud, the dolomitization of this mud, was thought "Must have taken place at, and not subsequent to, their deposition" p.212.

Bailey (in Clough et al, 1925) studied the same succession of the Ballagan Beds deposits in Glasgow area. In the type section, 100 distinct bands of cementstones were counted, in a sequence of these/

these beds about 70 metres thick. Their alternating character was considered as a rhythm attributed to a seasonal change which was believed to be of a geographical rather than climatic oscillation. It was noticed that the position of the Ballagan Beds sediments, is taken by volcanic rocks in the Garrel Burn with only a few intercalations of shale and cementstones present.

The Spout of Ballagan Sandstone, was the name given to the sandstone that overlies the Ballagan Beds in parts of their outcrops. The contact of the Ballagan Beds deposits with both sandstones above and below them, was considered to be gradational since they are found to interleave with each other, in a thickness of about 6 to 9 metres at these contacts. It was suggested that the cementstones were the product of chemical precipitation, in a land-locked lagoons, as a result of concentration of the waters, in these lagoons, during periods of drought.

Macgregor (1930) in his study of the Scottish Carboniferous Stratigraphy stated : "The picture, we thus gather of the physiographic conditions, under which the Cementstone Group of the Midland Valley was formed is that of a fringe of a continental area, before its submergence under the waters of the Carboniferous sea. It held a series of lagoons or sheets of brackish water, separated/

separated by land-barriers of older rocks, and subject to periodic desiccation; ..... The climate was arid or semi-arid, with infrequent but torrential rains, which renewed and extended the waters of the lagoons, and cut temporary out flows to the sea."

Muir et al (1956) described the cementstones as consisting of micrograined dolomite with varying proportion of angular detrital quartz, and argillaceous material. The CaO/MgO ratio for specimens analysed was found to vary between 1.3/1.0 and 2.4/1.0.

George (1958) suggested that the layered cementstones were in part chemically precipitated, as lagoonal deposits in hyper-saline pans of wide extent, but very shallow depth. Their marine origin was attributed to marine infiltration of these lagoons where evaporation, loss of carbon dioxide and desiccation were a constant feature. The cementstones were compared with dolomites of back-reef lagoons and the Zechstein sea.

Freshney (1961) studied the Ballagan Beds deposits on both sides of the Clyde, that is to say, Glasgow and Ayrshire regions. He believed the deposits to rest erosively on Upper Old Red Sand-stone. While the cementstones of Glasgow area were found devoid of any faunal content, those of the Ayr area contain a marine fauna of ostracods and brachiopods.

A shallow, semi-restricted evaporite lagoon was suggested as the environment of deposition, in which the cementstones accumulated/

accumulated as dolomitic or high magnesian marls and limestones. The assumed restricted connection of such lagoon with the open sea, is believed to be in the region of the North Channel between Northern Ireland and Scotland.

Current directions, heavy mineral assemblages, pebbles, and the presence of out-wash fan deposits in places, were used to derive the local palaeogeography. He envisaged a shore-line during the cementstones time to the north-west of Glasgow region, and in the south, along the line of the Straiton Fault and its extension north-east of Cumnock and north-west of Dailly.

Belt et al (1967) compared cementstones on both sides of the Atlantic, although they were found to be similar almost in every aspect, a non-marine environment of deposition, was proposed for the Canadian cementstones and a marginal to restricted marine environment for those of the British Isles.

Read (in Francis et al., 1970) investigated the Ballagan Beds deposits in Stirling District. Description of cores from Stirling No. 1 Bore, showed that the cementstones have irregular bases, and their contacts with the underlying and overlying shales is gradational. Brecciation is well displayed as fragments of relatively pure carbonate are found floating in a more argillaceous matrix. Cementstones in the bore proved to contain terrigenous material in excess of that present in those in the natural outcrops. Beds with terrigenous material concentrations in the form of laminae, contain/

contain obscured, thin-shelled spheroidal and vermiform bodies, which were considered of organic origin.

A rectilinear pattern of cracks, present in some beds, filled with either more sandy carbonate or coarse-grained carbonate, have been interpreted as being of desiccation origin.

Two types of nodules were identified, displacive and replacive, both, however, were considered of secondary origin. A secondary origin was also proposed for the layered cementstones in the bore but a primary one for those in the outcrop.

The sandstone that overlies the Ballagan Beds strata, was named the Downie's Loup Sandstone, which is equivalent to the Spout of Ballagan Sandstone in Glasgow area (Figure 1.2).

Browne (1980) studied the Ballagan Beds deposits, which he now calls the Ballagan Formation, in the Firth of Tay of Scotland. His work was concerned mainly with the study of data provided by five bore-holes, in which these sediments were encountered, small outcrops have also been investigated. The cementstones were divided into three main types, which are found to grade into one another, these are : Massive beds; laminated beds; and nodular beds. The Ballagan Formation was divided into three members, in ascending order, they are : Mains of Errol; Dron and Newburgh.

The/

The maximum thickness of an individual cementstone layer was found about 1.64 metres. Algal structures were rarely found present, while estheriids;ostracods; and Spirorbis were found present in some samples.

The cementstones were found to consist predominately of microcrystalline ferroan - dolomite, minor bands are composed exclusively of microcrystalline calcite. In the bedded varieties, the detrital material is present in the form of laminae and isolated grains, some of the latter appears to be etched.

1.4 The Research Problem

The review of the history of the previous work on the Ballagan Formation deposits, in the study area, indicates that the stratigraphy has been well studied. Almost all workers were satisfied with a brief description of the lithology, without intensive study of petrography and geochemistry. Geochemistry is a very important aspect of the work. Therefore, the chemical changes, both laterally and vertically in the sequence need to be investigated.

The present study concentrates mainly on the investigation of the petrography and geochemistry of the carbonates, in an attempt to reconstruct their original state and consequently, their depositional environment. In geochemistry, however, the bulk rock composition will be examined by the use of X-ray fluorescence and electron microprobe respectively. Studies of the diagenetic sequence will also be undertaken.

CHAPTER TWO

STRATIGRAPHY

The Ballagan Formation (Browne, 1980) known also as the Cementstone Group, constitutes the lower-most subdivision of the Calciferous Sandstone Measures (Macgregor, 1960). Its distribution in the western part of the Midland Valley of Scotland is shown in Figure 1.1, whereas its position in the Carboniferous succession is shown in Figure 1.2.

The formation consists of an alternation of lutites (mudstones and shales), which make up the highest proportion in terms of thickness, layered and nodular carbonates (slightly dolomitic limestones and calcitic dolomites, both argillaceous); and less common, sandstone.

2.1 The Base of the Ballagan Formation

The boundary between the Ballagan Formation and the Upper Old Red Sandstone deposits is transitional so that the identification of the base of the Ballagan Formation is extremely difficult (see also Young, 1860; Bailey in Clough et al, 1925; Mitchell and Mykura, 1962; and Read in Francis et al, 1970). Freshney (1961) faced the same problem in the Ayrshire areas.

Carbonates/

Carbonates, typical of the Ballagan Formation, interfinger with white sandstones at the base of the Ballagan Glen (Grid Ref. 572795) sequence. These white sandstones, some 6-9 metres thick furnish a passage zone linking the Upper Old Red Sandstone to the Carboniferous System (Bailey, in Clough et al, 1925, p.11). In the Auchenreoch Glen (Grid Ref. 420 773) section, this transitional zone is formed by an alternation of cornstones; lutites; and sandstone.

The Ballagan Formation is never found to rest on rocks older than the Upper Old Red Sandstone, but the existence of a minor disconformity between them, evidenced only by an eroded and weathered surface, at the top of the latter, occurs in parts of Ayrshire areas (Freshney, 1961, p.2-3). However, Waterston (1965) believes that part of the Upper Old Red Sandstone is of Carboniferous age.

The boundary between the Ballagan Formation and the Upper Old Red Sandstone is transitional, and is arbitrarily taken at the occurrence of the first carbonate bed of Ballagan Formation type. Francis (1965); Read (in Francis et al, 1970) used the same criteria.

2.2/

2.2 The Top of the Ballagan Formation

The top of the Ballagan Formation, as with the base, is poorly exposed. It is in places capped by the Spout of Ballagan Sandstone (Bailey, in Clough et al, 1925), or its equivalent, the Downie's Loup Sandstone (Read, in Francis et al, 1970). On the south slope of the Campsie Fells, it is found overlain, and occasionally interleaving with igneous rocks of the Clyde Plateau Lavas, which replaces it almost completely, and rest on the Upper Old Red Sandstone, as in the Garrel Burn (Grid Ref. 705 800), near Kilsyth (Bailey, in Clough et al, 1925).

In most parts of the Western Midland Valley, the first appearance of lavas, or at least of ashes of the Clyde Plateau Lavas, is taken to mark the base of the Upper Calciferous Sandstone Group (Freshney, 1961).

The formation and the overlying sandstone are found both exposed in the study area at the following exposures: Gargunnock Burn; Little Corrie; and Ballagan Glen.

2.3 Faunas, Floras and Age

The Ballagan Formation is generally deficient in fossils. However, plant remains and fish scales were found in Auchenreoch Glen (Young 1860). Ostracods and Spirorbis were reported by Freshney (1961) in Ayrshire. Algal structures; Spirorbis, ostracods; and fish/

fish scales and teeth; and thin-shelled bodies were found by Francis and Read (in Francis et al, 1970). Similar assemblages were reported by Browne (1980) in the Firth of Tay.

On the grounds of spore assemblages recovered from the Ballagan Formation sediments, an Upper Tournaisian and a Lower Visean age is deduced (Sullivan, 1968; Neeves et al, 1973).

2.4 Study Area and General Description of Lithologies

The present investigation covers the area located between Glasgow: Stirling and Greenock, namely, the Glasgow region, or the northwest of the Midland Valley of Scotland. Although the outcrop of the Ballagan Formation strata is generally discontinuous, excellent exposures occur where detailed study can be undertaken (Figure 1.1).

Field investigation of the following exposures was carried out: Loch Thom (Grid Ref. 256 708); Ben Bowie (Grid Ref. 340 830), near Helensburgh; Auchenreoch Glen (Grid Ref. 420 773), near Dumbarton; Overtoun Burn (Grid Ref. 426 765), also near Dumbarton; Ballagan Glen (Grid Ref. 572 795), near Strathblane; Little Corrie (Grid Ref. 578 850), near Fintry; and Gargunnock Burn (Grid Ref. 707 930), near Gargunnock.

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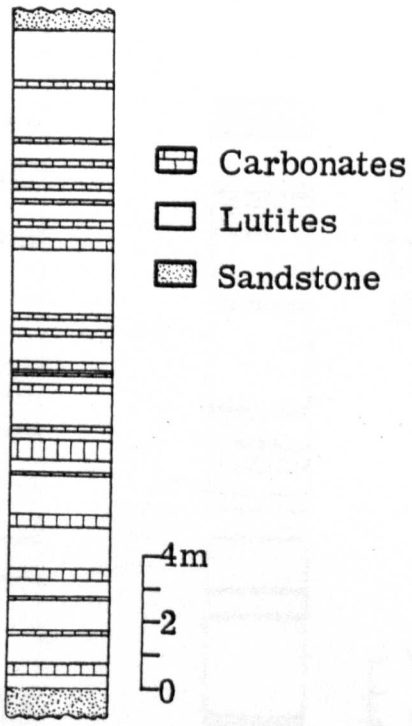

Fig. 2.1 : Columnar section of the exposed portion of Ballagan Formation. Loch Thom

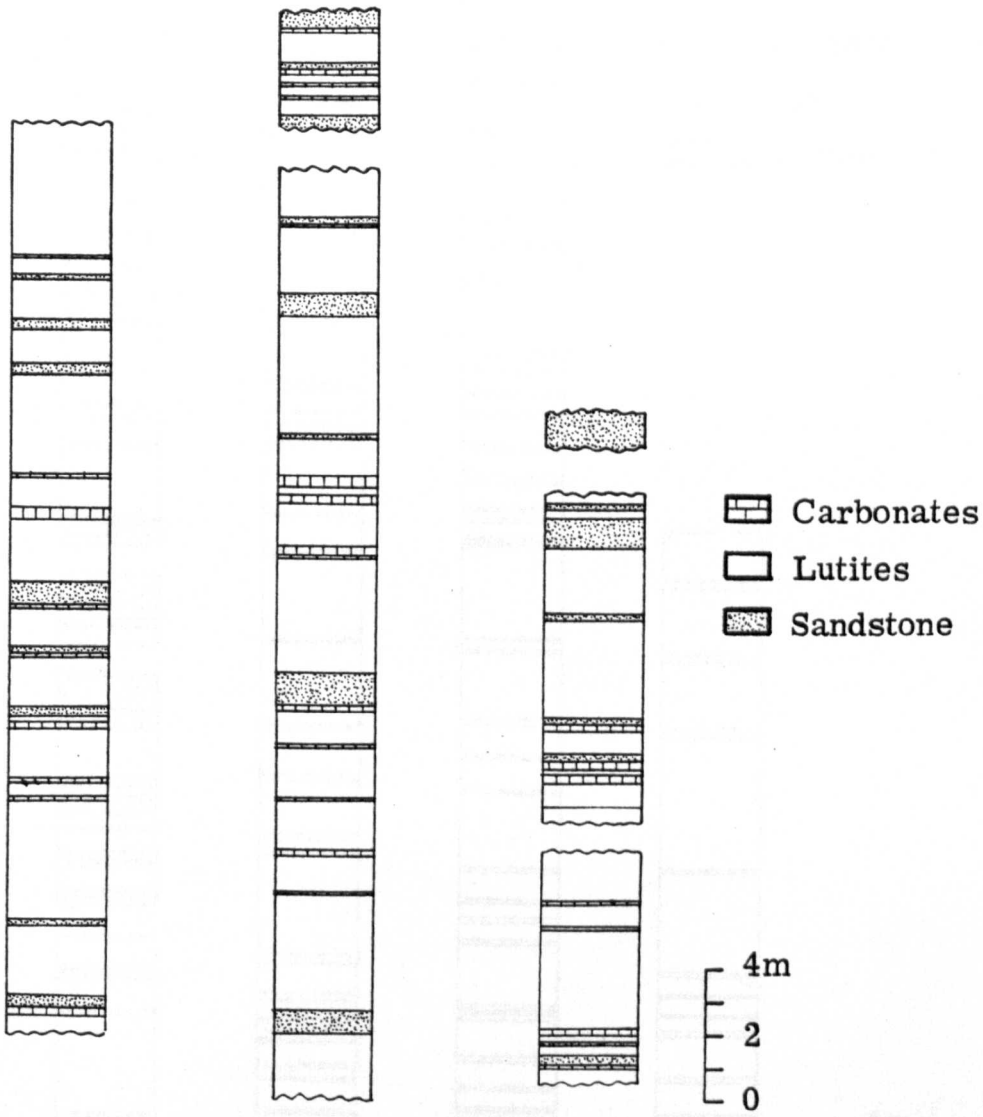

Fig. 2. 2 : Columnar section of the exposed portion of Ballagan Formation. Base to top from left to right. Ben Bowie, near Helensburgh.

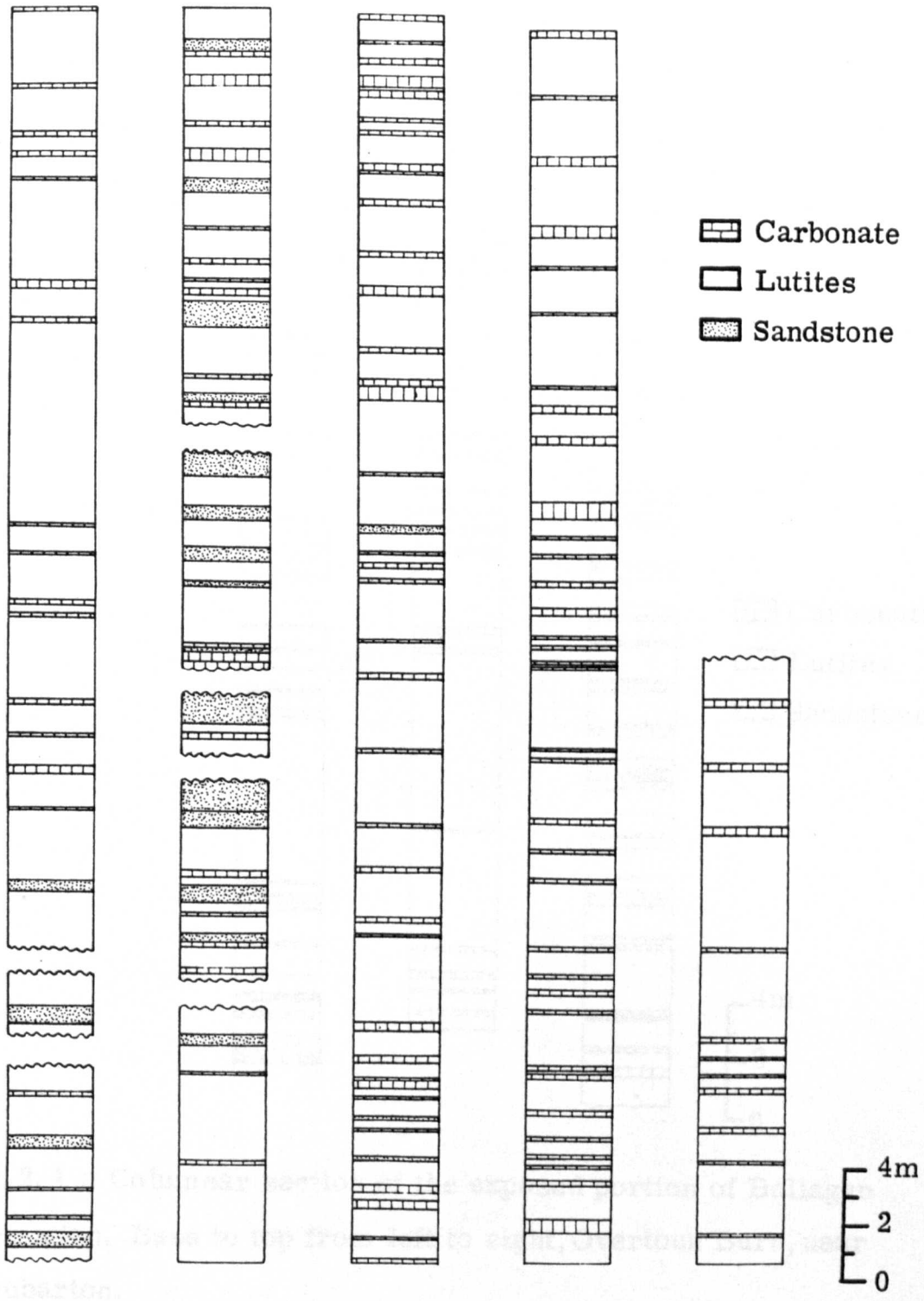

Fig. 2.3 : Columnar section of the exposed portion of Ballagan Formation. Base to top from left to right. Auchenreoch Glen, near Dumbarton.

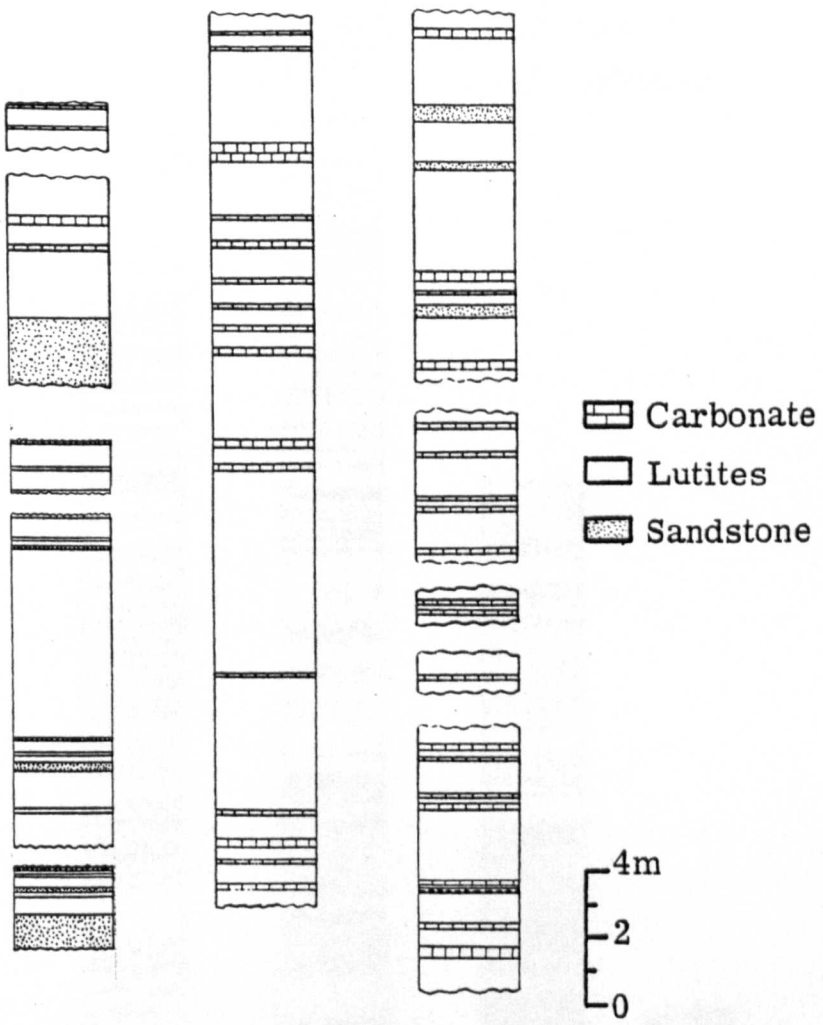

Fig. 2.4 : Columnar section of the exposed portion of Ballagan Formation. Base to top from left to right, Overtoun Burn, near Dumbarton.

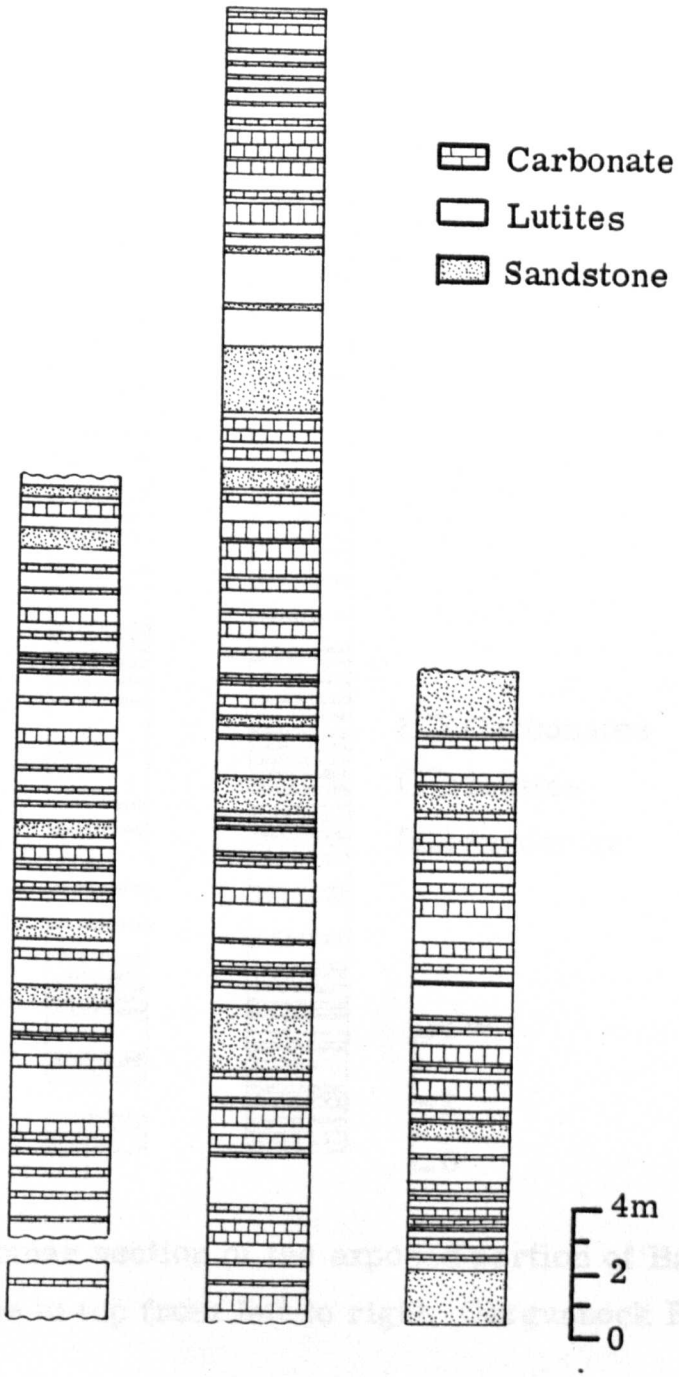

Fig. 2.5 : Columnar section of the exposed portion of Ballagan formation. Base to top from left to right. Ballagan Glen, near Strathblane.

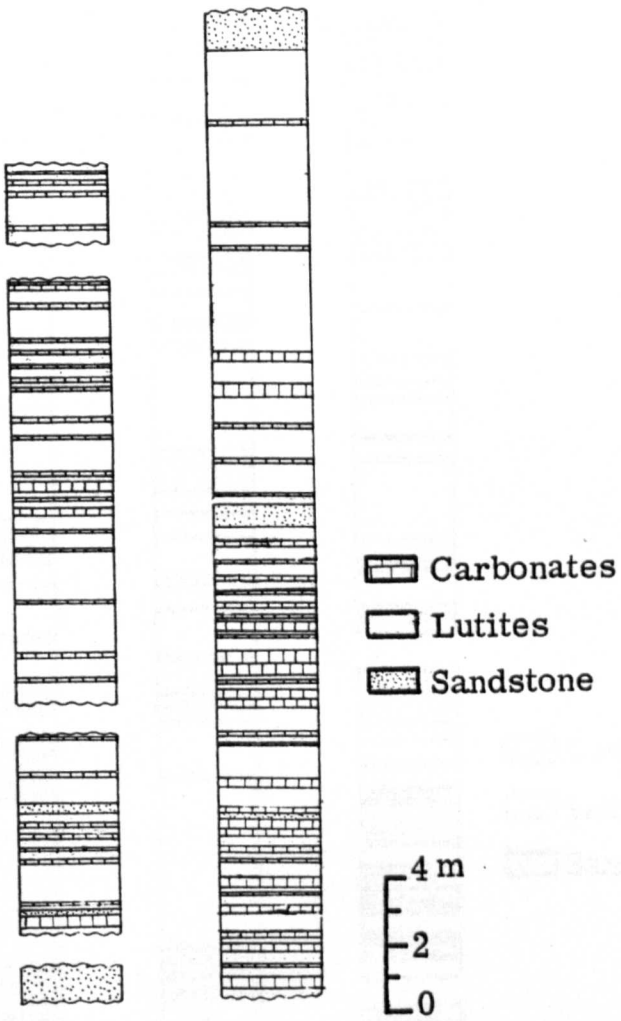

Fig. 2.6 : Columnar section of the exposed portion of Ballagan Formation. Base to top from left to right. Gargunnock Burn, Gargunnock.

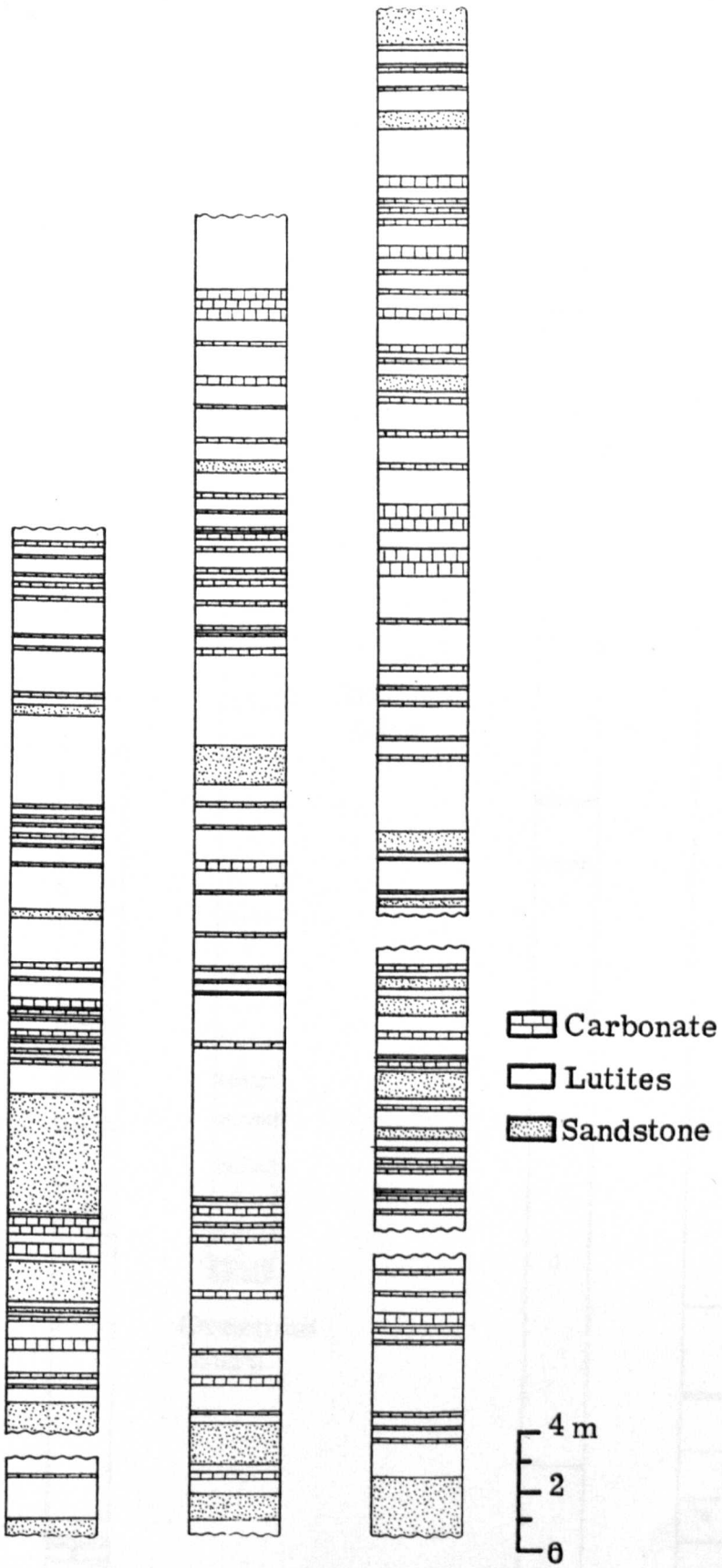

Fig. 2.7 : Columnar section of the exposed portion of Ballagan Formation. Base to top from left to right. Little Corrie, near Fintry

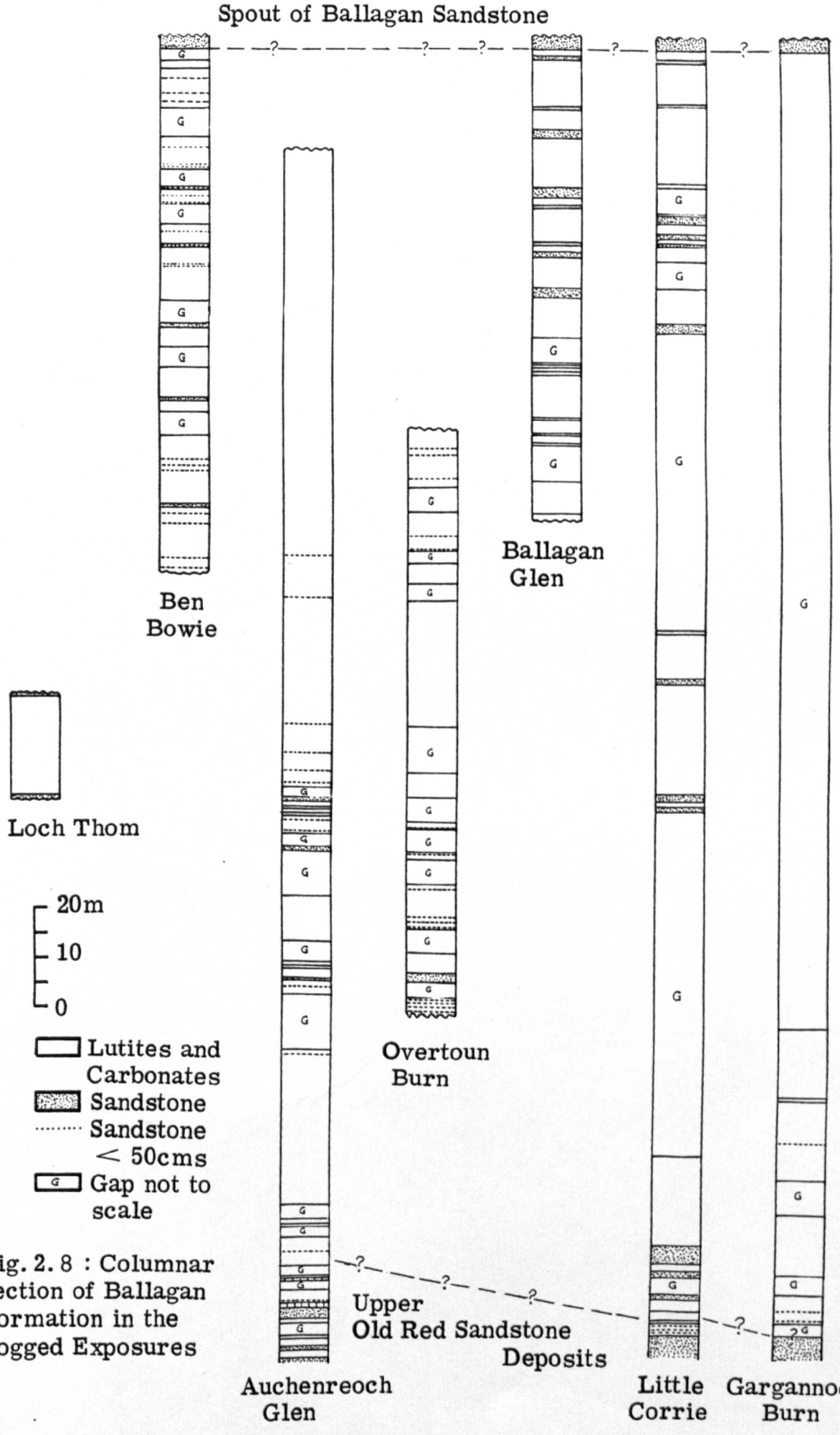

Fig. 2. 8 : Columnar Section of Ballagan Formation in the Logged Exposures

Plate 2.1

Photograph showing lateral replacement of stratified by nodular carbonates

Auchenreoch Glen, near Dumbarton.

The maximum known thickness of the formation occurs at Auchenreoch Glen section, where about 194 metres of strata were measured. The maximum true thickness is certainly greater and is estimated at about 400 metres as indicated on the maps of the Geological Survey, Scotland (Stirling Sheet, scale 1: 50,000). The minimum known thickness occurs at Loch Thom, where only about 21 metres are exposed. The measured thicknesses are shown in Figures 2.1-7.

Correlation between the different exposures proved extremely difficult. Therefore, Figure 2.8 has been prepared for the purpose of comparison with respect to the exposed thickness.

The Ballagan Formation is informally divisible into a lower and an upper division, based principally on sandstone recurrence and lutites bed thickness. The lower division is characterized by a relative abundance of sandstone horizons, and a wide-range of lutites bed thickness. The upper division contains minor sandstone beds, and shows a relatively narrow range of lutites bed thickness.

The carbonate (cementstone) layers are naturally divided into two types, stratified and nodular. The morphological similarities of these carbonates have contributed substantially to the difficulty experienced in lateral correlation. In some instances, both nodular and stratified types occur in the same level (Plate 2.1).

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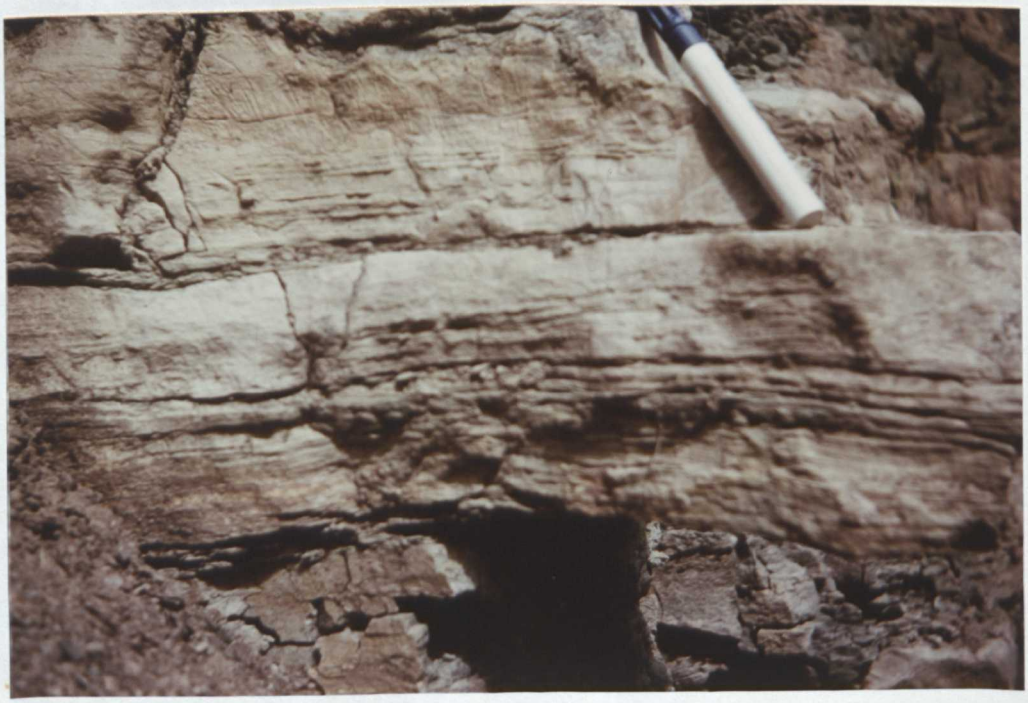


Plate 2.2

Upper: Photograph showing carbonate layer overlain by sandstone.

Auchenreoch Glen, near Dumbarton.

Lower: Photograph showing laminations developed by concentration of sand particles.

Gargunnock Burn, Gargunnock.

The carbonates, weathering greyish to yellowish, are generally grey in colour. Some brown-reddish units occur in association with lutites of similar colour, which may indicate the secondary origin of this colour. They are generally either flinty or sucrosic in texture. Brecciated layers are rare to common.

The thickness of individual carbonate layers is generally under 0.40 metre, slightly thicker occurrences, however, are recorded occasionally. The average of the arithmetic mean of their thickness is 0.18 metre with a Standard Deviation of 0.12 metre.

The nodules measure up to 0.35 metre in thickness(perpendicular to the bedding), and up to 0.40 metre in length. They are bulbous, semispherical, discoidal, and generally irregular in shape.

The boundaries with the enclosing lutites are generally irregular, but sharp with the exception of those of the brecciated horizons, which are gradational. Carbonates are occasionally found in contact with sandstone, this contact has always been sharp and irregular (Plate 2.2). Stratification developed by concentrations of sandy material are of very rare occurrence (Plate 2.3). Shrinkage cracks are found to be a common feature in the carbonate layers in general, the stratified ones in particular (Plates 4.1 and 4.2).

The carbonates are next to the lutites in total thickness proportion as well as number of occurrence throughout the area.

The/

The lutites (mudstones and shales) show no fissility. They vary in colour from green to grey to black, occasionally having a blue tint, less common, brown-reddish, which increases towards the top as in Ballagan Glen section. The lutites actually constitute the highest proportion of the strata thickness in every exposure.

Gypsum, pink to reddish-brown in colour commonly occurs in the form of thin, horizontal as well as subvertical to vertical sheets, presumably filling joints in the lutites. The occurrence of white fibrous gypsum has been recorded only in the Ballagan Glen section, where a layer of about 0.05 metre in thickness is found enclosed into blackish lutites. Many layers of gypsum in shales are known from a tunnel section in Dumbarton Muir (Bluck, personal communication).

The sandstones are mainly white arenites, with some minor amounts of feldspar. The thick sandstones at the base of the sequence, at Auchenreoch Glen, contain sand pseudomorphs after halite, whereas in the thinner sandstones, fish scales and teeth have been found (Bluck, personal communication). The sandstones are either flat stratified with lineation developed, cross-stratified, or rippled. They form less than 15% of the formation thickness at their maximum occurrence.

CHAPTER THREE

PETROGRAPHY

3.1 General Description

The carbonate beds of the Ballagan Formation comprise crystals ranging in size from cryptocrystalline to microcrystalline, and less common, fine crystalline. The fine crystals are anhedral in shape and display a chicken-wire texture, whereas the rest are subhedral to euhedral and show sucrosic texture. These sediments are mainly mudstones in Dunham's (1962) classification as the crystal size is generally less than 20 microns.

The carbonate beds contain variable amounts of terrigenous material. They show a transition from almost pure carbonates up to those with a very high terrigenous content. This material is composed predominantly of clay minerals, with less abundant, scattered quartz particles, of various shapes and sizes, feldspar is of minor occurrence. The latter two constitute a considerable proportion of this material in some cases.

Although the carbonates are naturally divided into two categories, stratified and nodular, further lithological subdivision is found possible. They can be subdivided into three major lithological groups, on the basis of the size of the constituent carbonate grains (crystals). For matter of convenience, these subdivisions/

subdivisions will be referred to in the text as Microfacies A, B and C, and these are :

1. Microfacies A : Cryptocrystalline
2. Microfacies B : Microcrystalline to very finely crystalline
3. Microfacies C : Finely crystalline

Distinction between these microfacies, in some cases, has proved to be difficult, especially when Microfacies A and B were involved. This difficulty, however, is thought to be due to the fact that the crystal-size found to be of an overlapping nature, as it is determined by diagenesis and that fine crystalline carbonates are variously replaced by coarser. However, Microfacies A comprises crystals under 5 microns, whereas Microfacies B comprises crystals over 5 microns. Therefore, the assignment of any carbonate bed to either microfacies will be determined by the crystal-size that occupies wider area in the representative thin-section. Plate 3.7 shows an intermediate fabric between Microfacies A and B.

3.2 Description of Microfacies

1. Microfacies A

Microfacies A comprises mainly a cryptocrystalline fabric of dolomite (Plate 3.1). The crystals are generally indistinguishable by the use of an ordinary petrographic microscope, but where identifiable, these crystals are found to measure less than 5 microns/

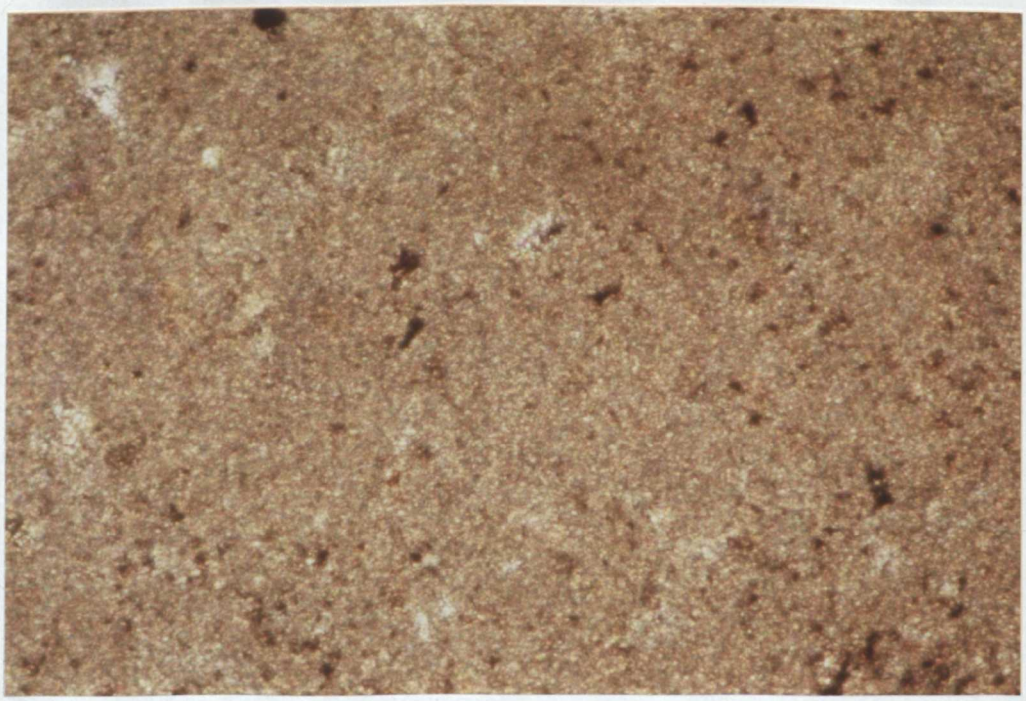


Plate 3.1

Upper: Microphotograph showing the fabric of Microfacies A, Nodular. Under crossed nicols. Mag. 40X.

Overtoun Burn, near Dumbarton.

Lower: Microphotograph showing the fabric of Microfacies A, Stratified. Under crossed nicols. Mag. 40X.

Little Corrie, near Fintry.

microns in diameter, which is set as an upper limit for the crystals belonging to this microfacies.

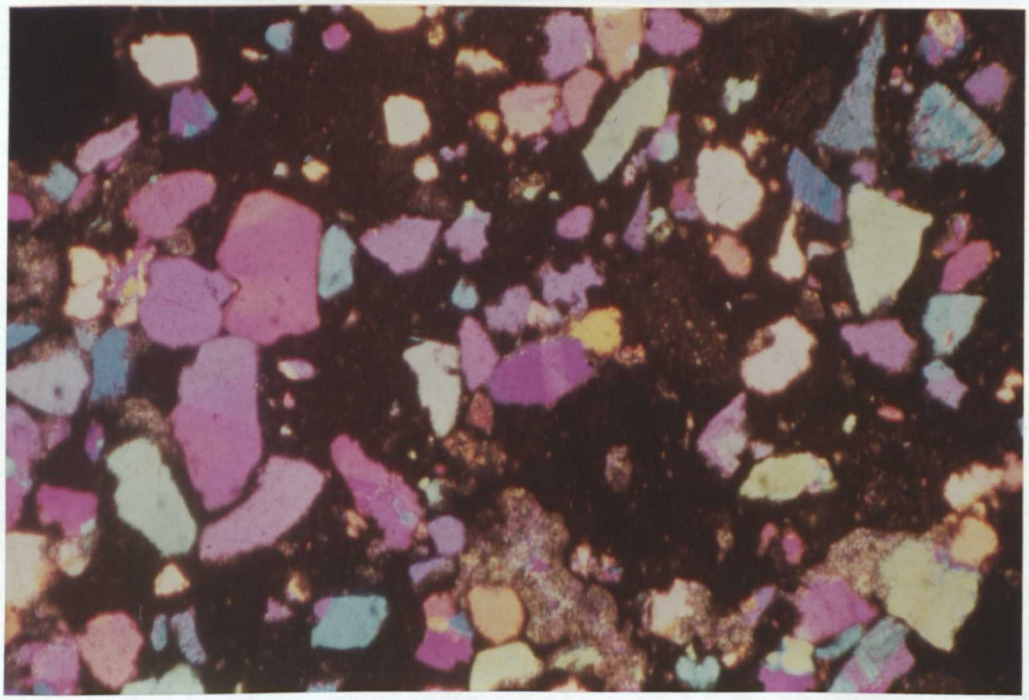
Microfacies A contains appreciable amounts of terrigenous material, which consists predominantly of clay with common quartz - sand, and less common, feldspar particles.

The sand portion is found generally as randomly distributed grains (Plate 3.2), which because of the absence of lamination are believed to be of wind-blown origin. In marked contrast sandy lenticles and laminae (Plate 3.2) with dolomite matrix and/or calcite cement are less common, these are believed to be of bottom traction currents origin. The sand particles vary both in shape and size, some of them appear to be replaced by a relatively coarser crystalline rim (Plate 3.3). The clay portion, however, is considered responsible for most of the turbidity of the dolomite crystals in this microfacies, Braithwaite (1966); and Browne (1980) attributed the clouded appearance of crystals to the same phenomenon.

This microfacies contains gypsum as a primary sediment, which has been partially replaced by calcite (Plate 3.4). Laminations which resemble these developed by algae occur in many thin sections (Plate 3.5). In most slides the microfacies has to a variable extent a blocky and brecciated appearance most likely produced by the brecciation of algal material.

Electron microprobe analyses of Microfacies A are shown in Tables 6.9 and 6.10. These analyses indicate that the dolomite crystals are rather impure. This result supports the assumption made earlier with respect to the turbidity of the dolomite crystals.

In/



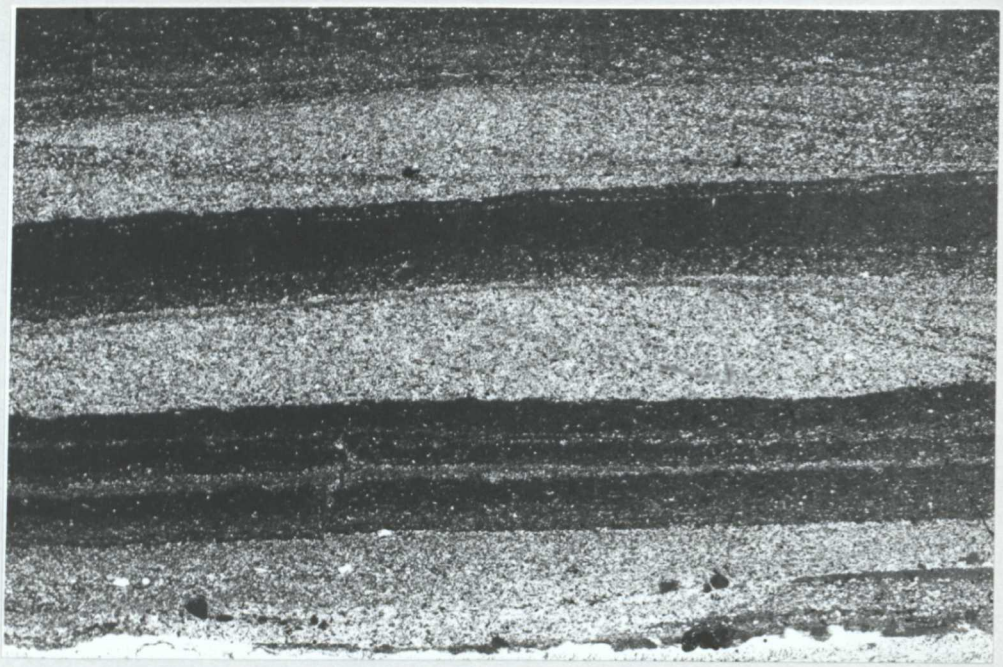


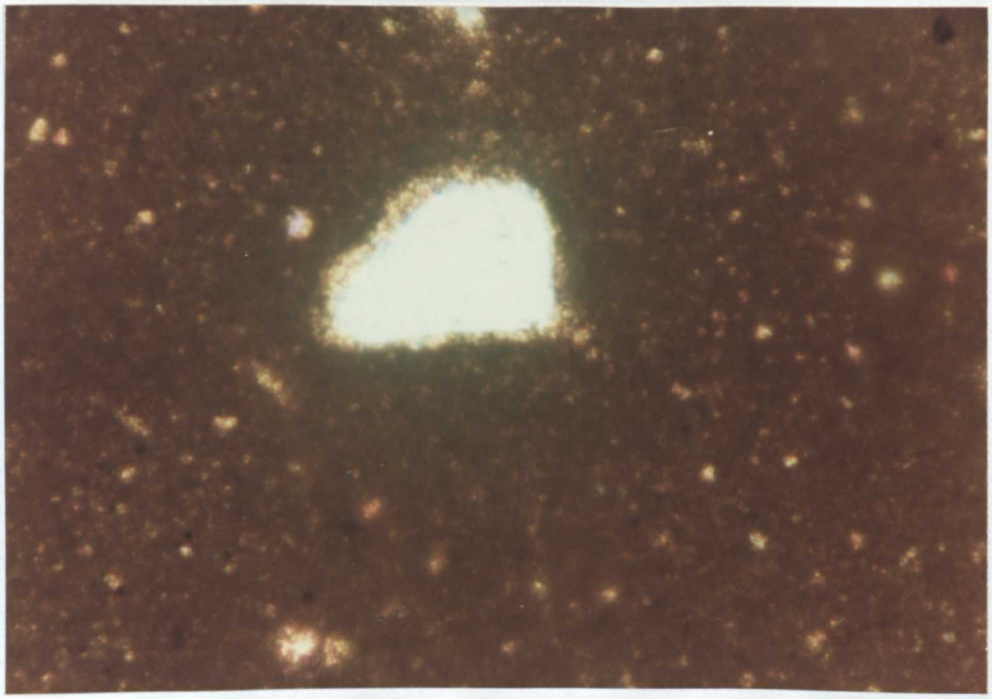
Plate 3.2

Upper: Microphotograph showing the distribution (occurrence) of sand particles in Microfacied A. Under crossed nicols. Mag. 10X.

Loch Thom.

Lower: Photograph of a thin section showing sandy laminae in Microfacies A. Dark laminae are carbonates. Mag. 8X.

Gargunnock Burn, Gargunnock.



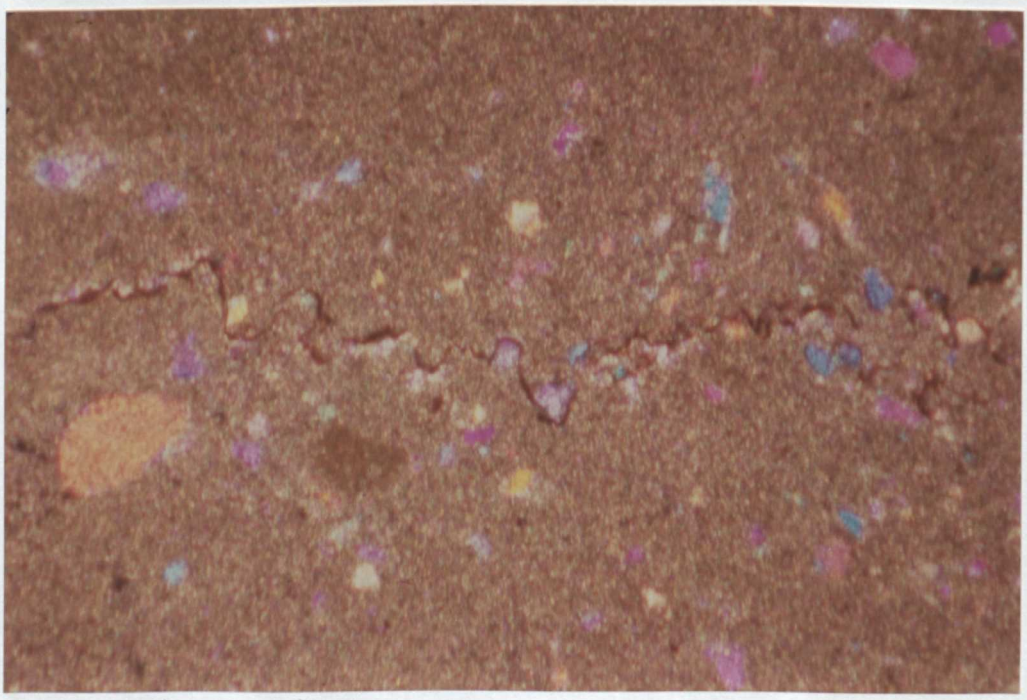


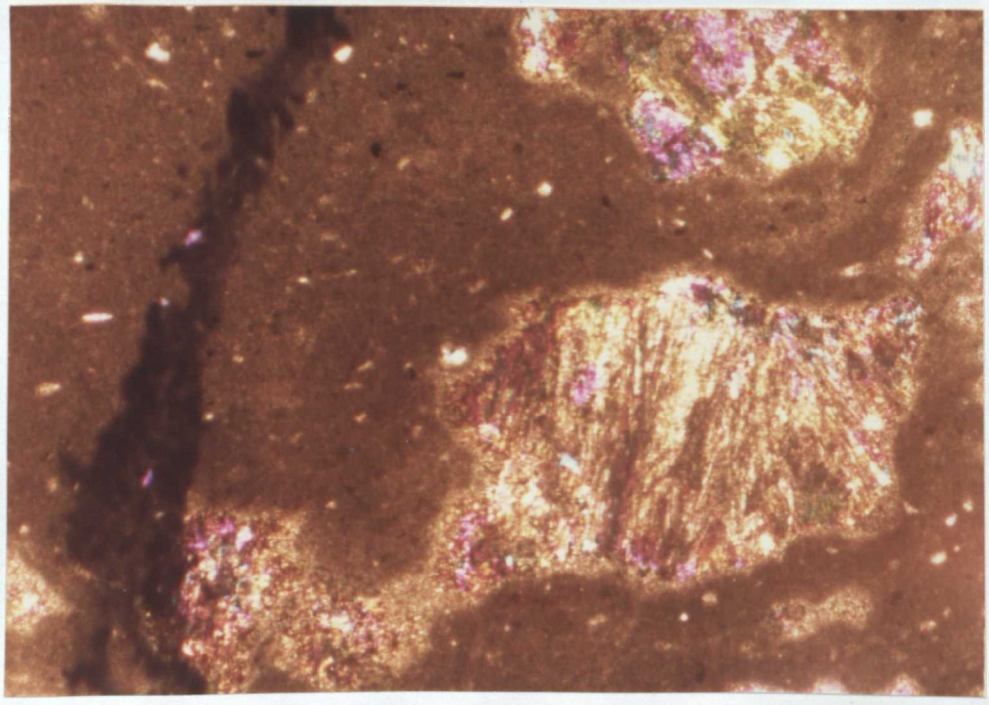
Plate 3.3

Upper: Microphotograph showing etched sand grain, Micro-facies A. Under crossed nicols. Mag. 40X.

Overtoun Burn, near Dumbarton.

Lower: Microphotograph showing the occurrence of stylolites. Under crossed nicols. Mag. 10X.

Auchenreoch Glen, near Dumbarton.



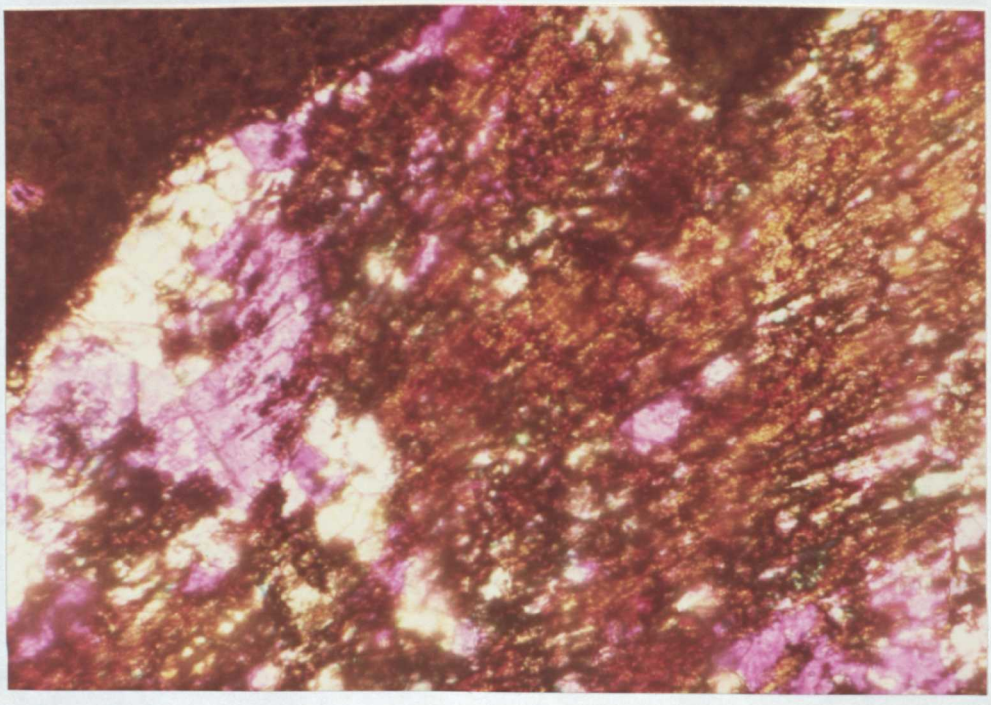


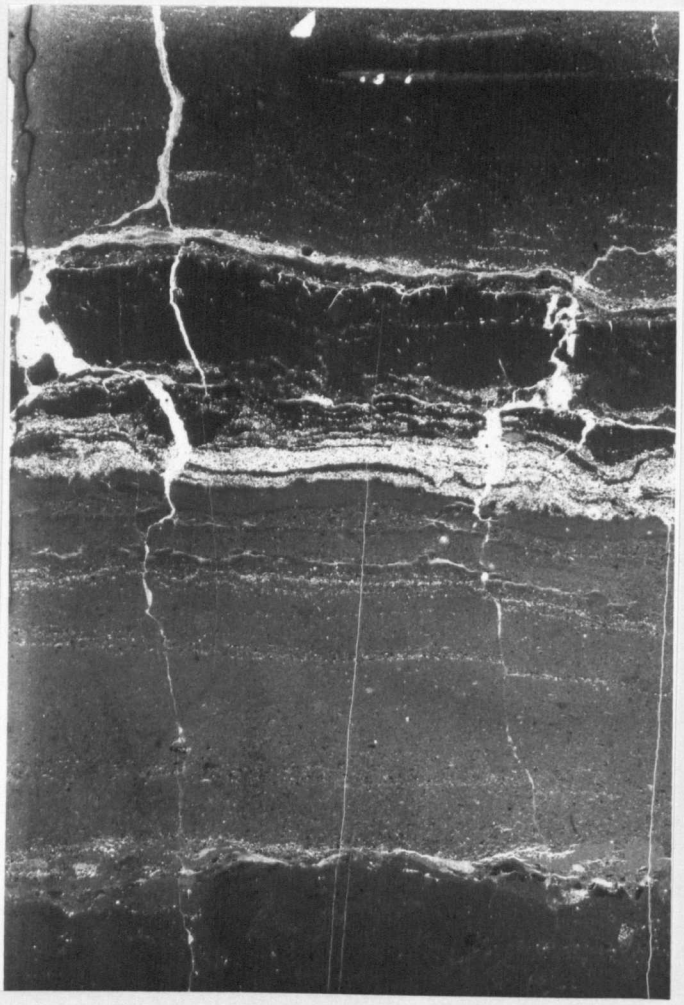
Plate 3.4

Upper: Microphotograph showing original gypsum in Microfacies A. Under crossed nicols. Mag. 10X.

Ballagan Glen, near Strathblane.

Lower: Microphotograph showing original gypsum in Microfacies A partially replaced by calcite (purple colour) mainly to the left. Under crossed nicols. Mag. 25X.

Overtoun Burn, near Dumbarton.



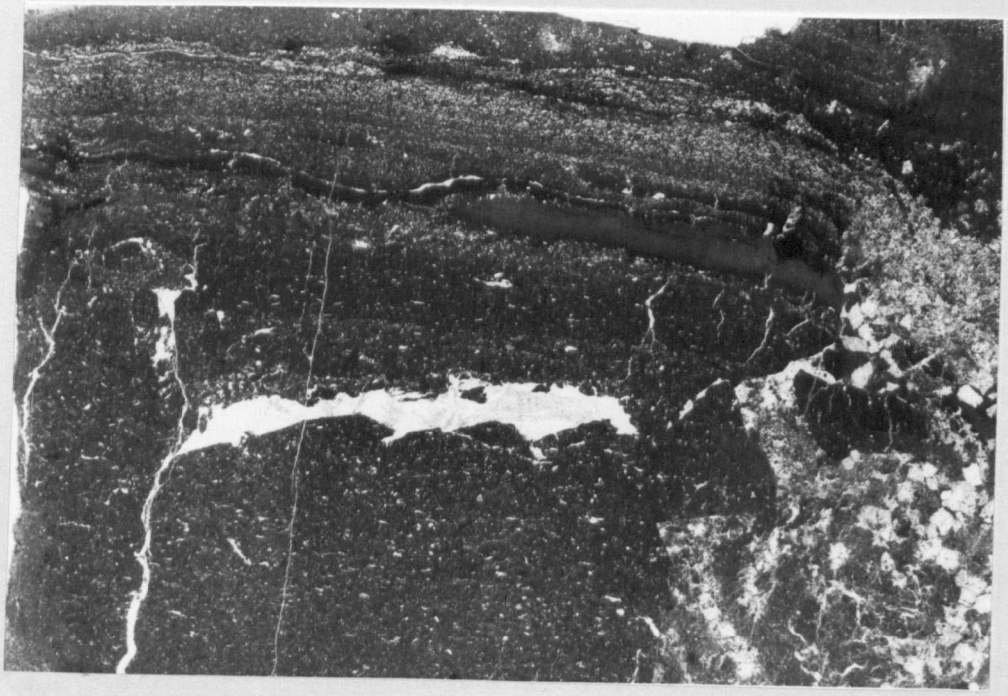


Plate 3.5

Upper: Photograph of thin section showing structure resembling algal laminations, Microfacies A. Mag. 5X.

Ballagan Glen, near Strathblane.

Lower: As above.

Gargunnock Burn, Gargunnock.

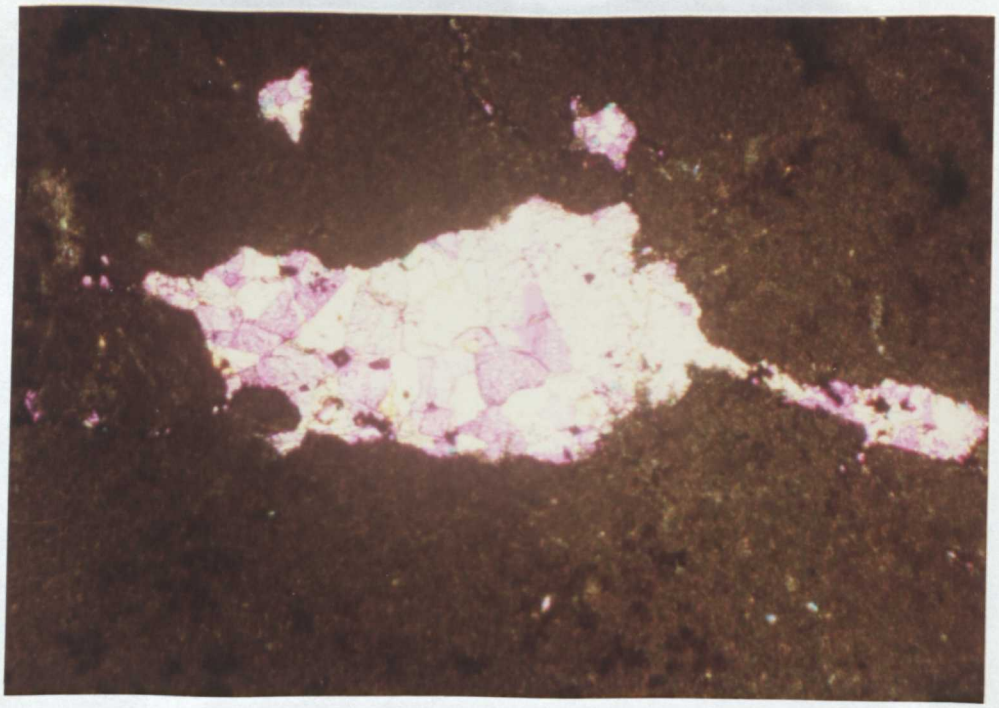
In addition to being the finest in crystal-size, this microfacies is characterized by the common occurrence of cavities (Plate 3.6) whereas veinlets are rare and relatively tiny, and usually occur in the coarser portion. Poorly developed stylolites are of rare occurrence (Plate 3.3).

Microfacies A is found represented in both the stratified and the nodular carbonate beds (Figs. 3.6-8). It forms approximately between 38 and 62 percent of the carbonates in the Ballagan Formation.

2 Microfacies B

Microfacies B consists predominantly of microcrystalline to very finely crystalline, subhedral to euhedral, aggregates of dolomite crystals displaying a sucrosic texture (Plate 3.8). These crystals are derived from a finer fabric, presently they generally fall between 5 and 15 microns in diameter, but may reach a diameter up to 30 microns. Still coarser mosaics also occur, but on a relatively minor scale.

Microfacies B contains comparatively less quartz material than Microfacies A. As the dolomite crystals appear slightly clearer, the clay may have concentrated more substantially in the intercrystalline boundaries. These boundaries are better developed and look rather dark. This is a consequence of the process of recrystallization/



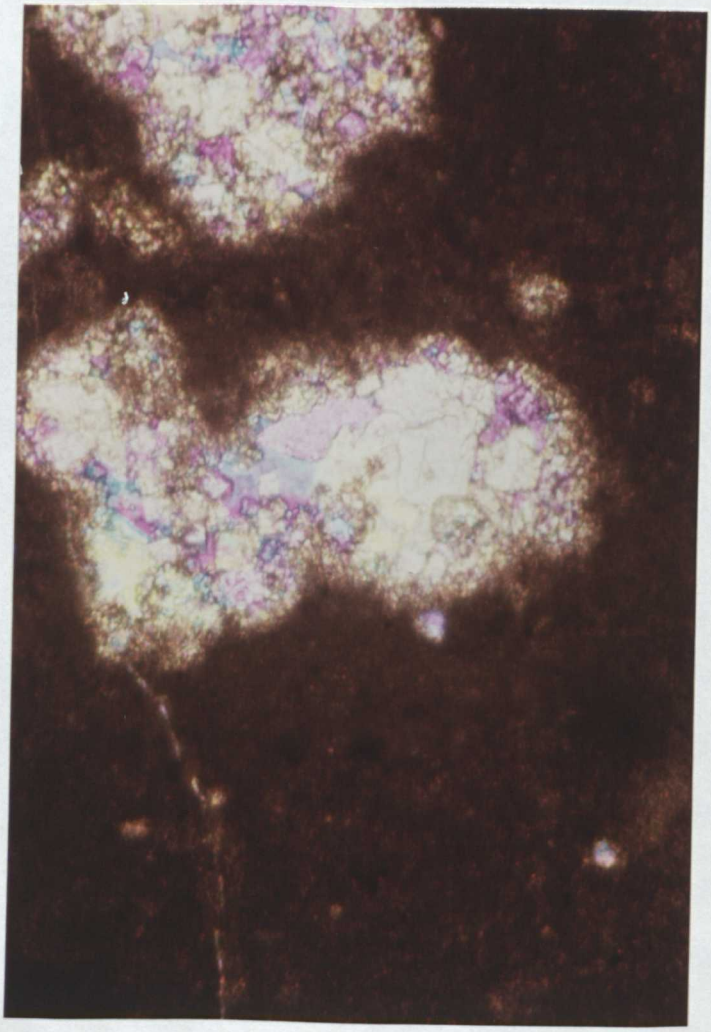


Plate 3.6

Upper: Microphotograph showing calcite cavity-cement. Under crossed nicols. Mag. 10X.

Overtoun Burn, near Dumbarton.

Lower: Microphotograph showing calcite cavity-cement with gypsum (bluish). Under crossed nicols. Mag. 25X.

Ballagan Glen, near Strathblane.

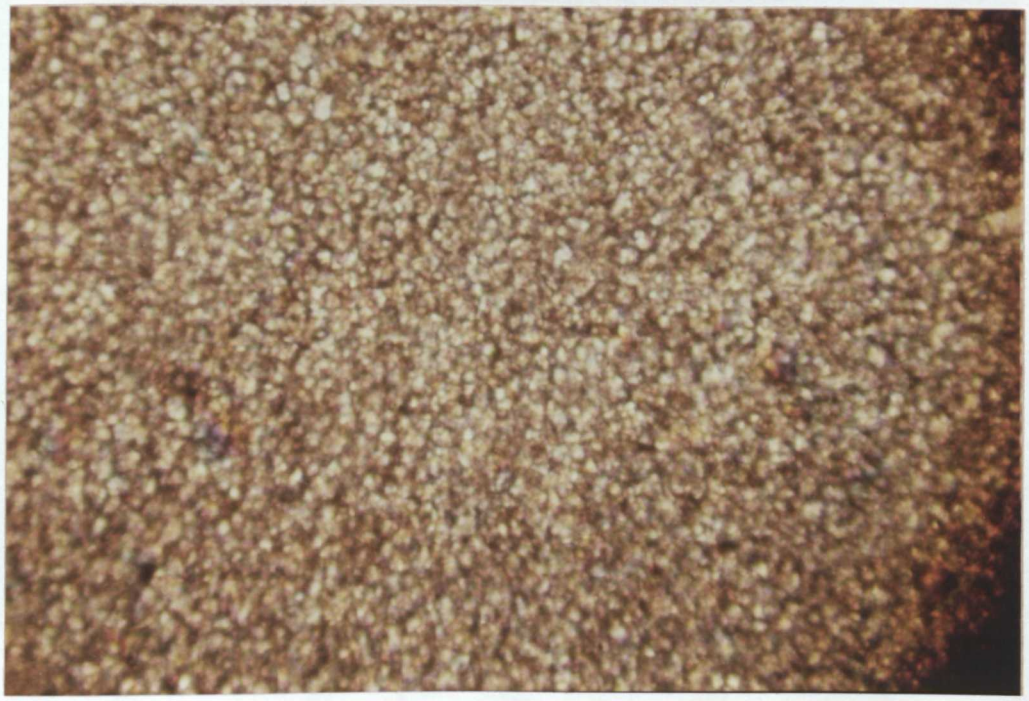
Plate 3.7

Upper: Microphotograph showing an intermediate fabric between Microfacieds A and B, Nodular. Under crossed nicols. Mag. 40X.

Overtoun Burn, near Dumbarton.

Lower: As above, Stratified.

Overtoun Burn, near Dumbarton.



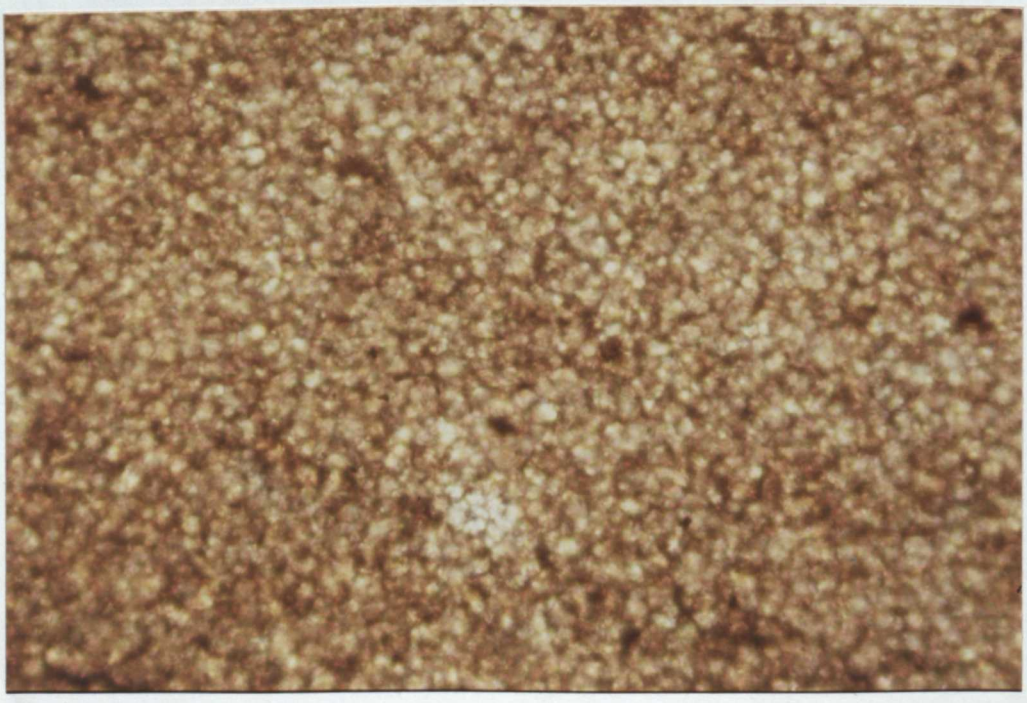


Plate 3.8

Upper: Microphotograph showing the fabric of Microfacies B, Nodular. Under crossed nicols. Mag. 40X.

Gargunnock Burn, Gargunnock.

Lower: As above, Stratified.

Overtoun Burn, near Dumbarton.

recrystallization, by which clay, included in the original dolomite crystals, was partially expelled to the periphery of the newly formed crystals (Table 6.12). Folk (1965) ascribed part of the translucency of microspar to the possibility of expulsion of impurities to the grain boundaries leaving the grains themselves more translucent. Representative electron microprobe analyses are shown in Tables 6.11 and 6.13-15. These analyses indicate the relative purity of dolomite crystals which supports the proposal made above regarding expulsion of clay during neomorphism.

Microfacies B is characterized by the relative uniformity of its crystal-size; the virtual absence of cavities; and its ground-mass being traversed by a net-work of veinlets, of various sizes and compositions.

This microfacies has developed indiscriminately in both stratified and nodular carbonates (Figs. 3.6-12). It forms approximately between 24 and 51 percent of the carbonate beds of the Ballagan Formation. A proposed model for its development is shown in Fig. 3.1.

3. Microfacies C

Microfacies C comprises anhedral, interlocking crystals exhibiting a chicken-wire texture (Plate 3.9). These crystals generally measure between 50 and 150 microns in their longest diameter/

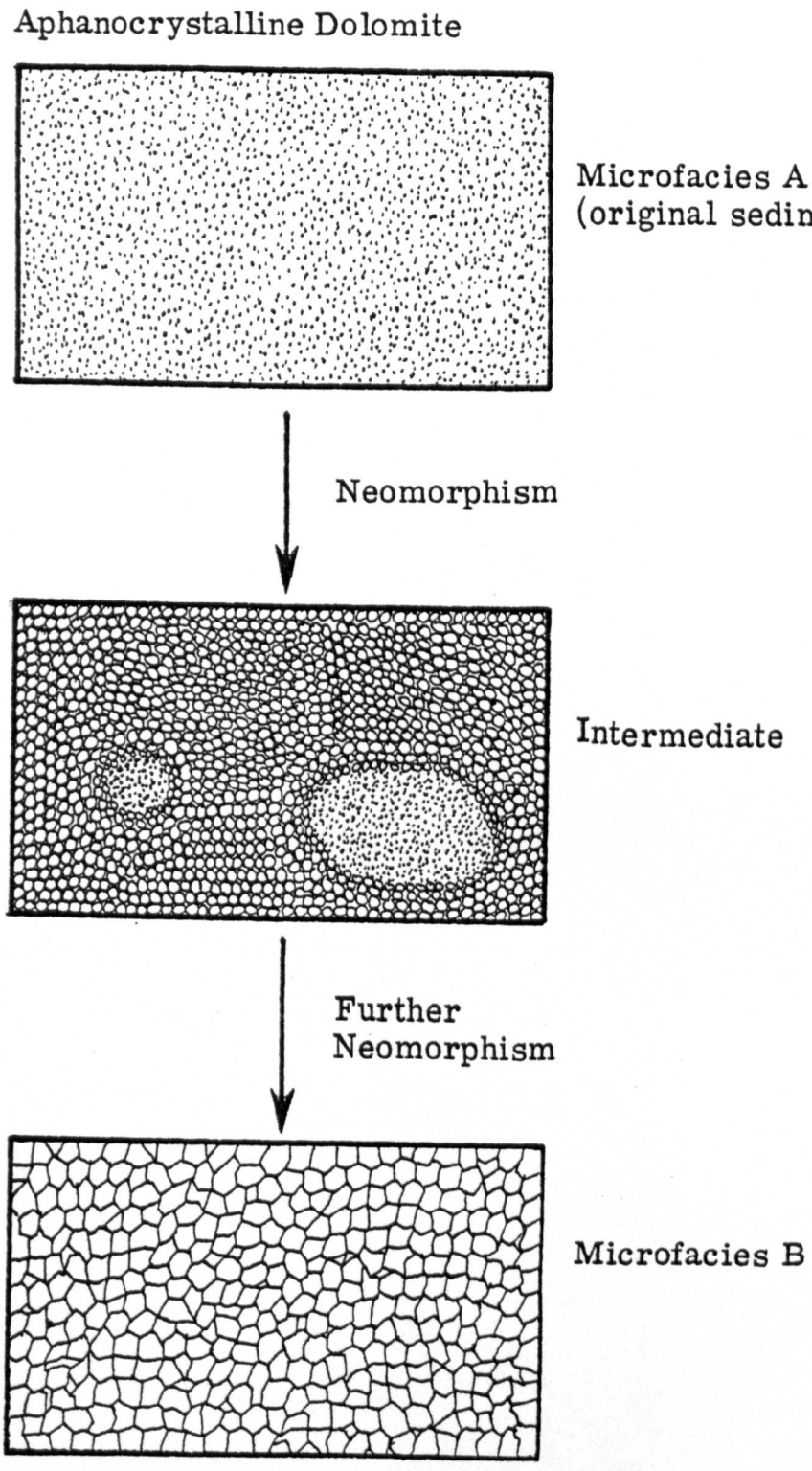
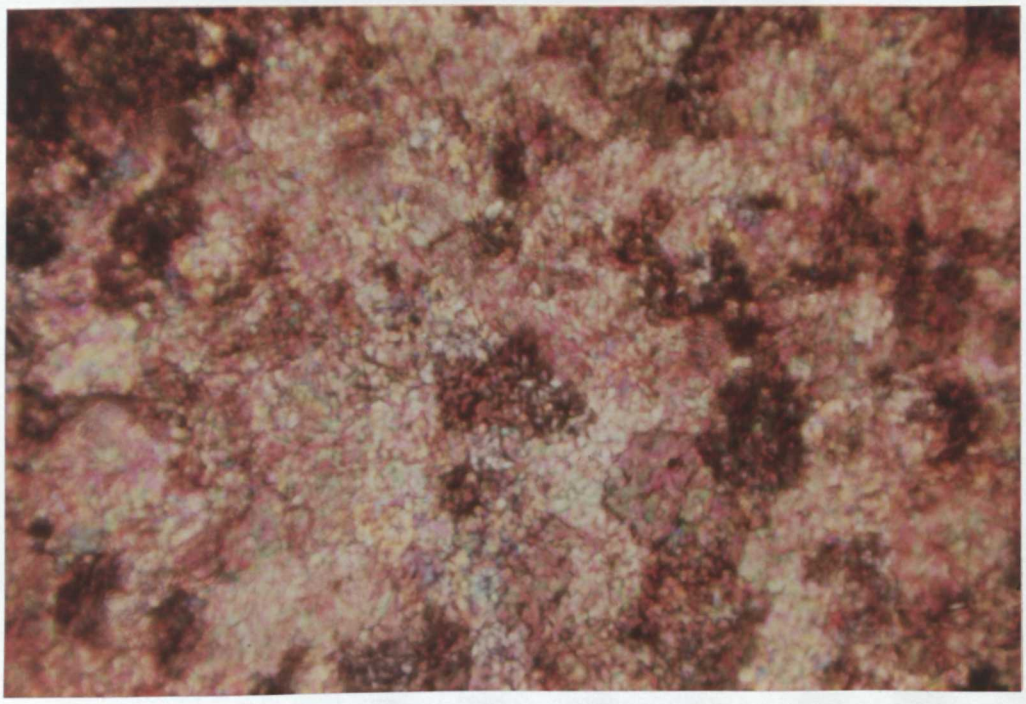


Fig. 3.1 : Stages of neomorphism in formation of Microfacies B from Microfacies A. Not to scale.



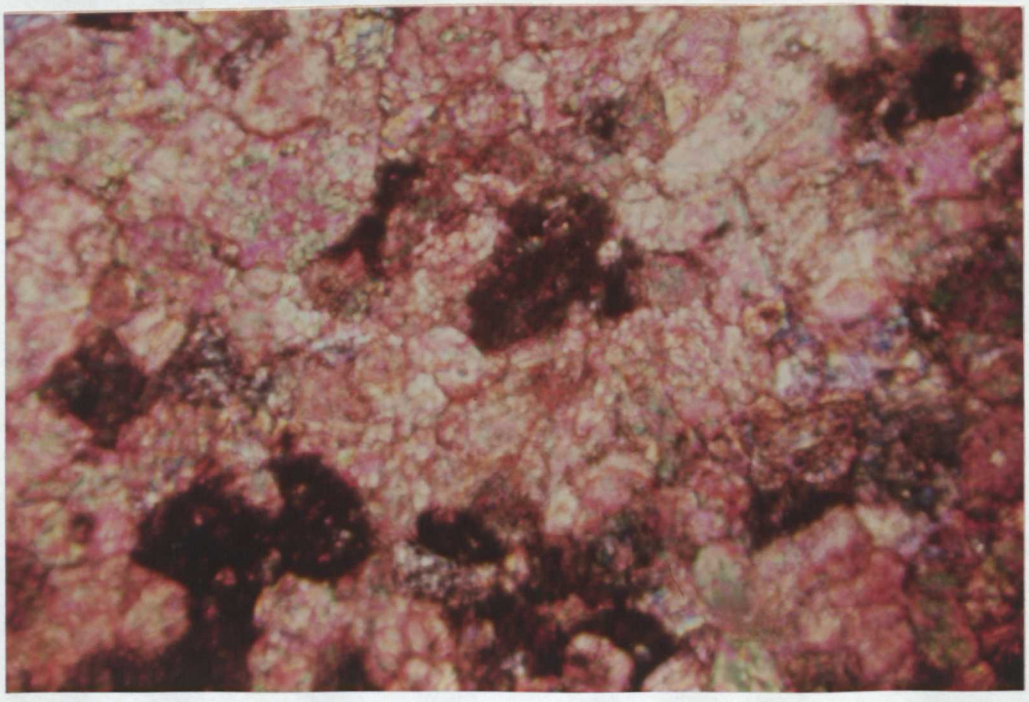


Plate 3.9

Upper: Microphotograph showing the fabric of Microfacies C, Stratified. Under crossed nicols. Mag. 40X.

Little Corrie, near Fintry.

Lower: As above, Pseudobrecciated.

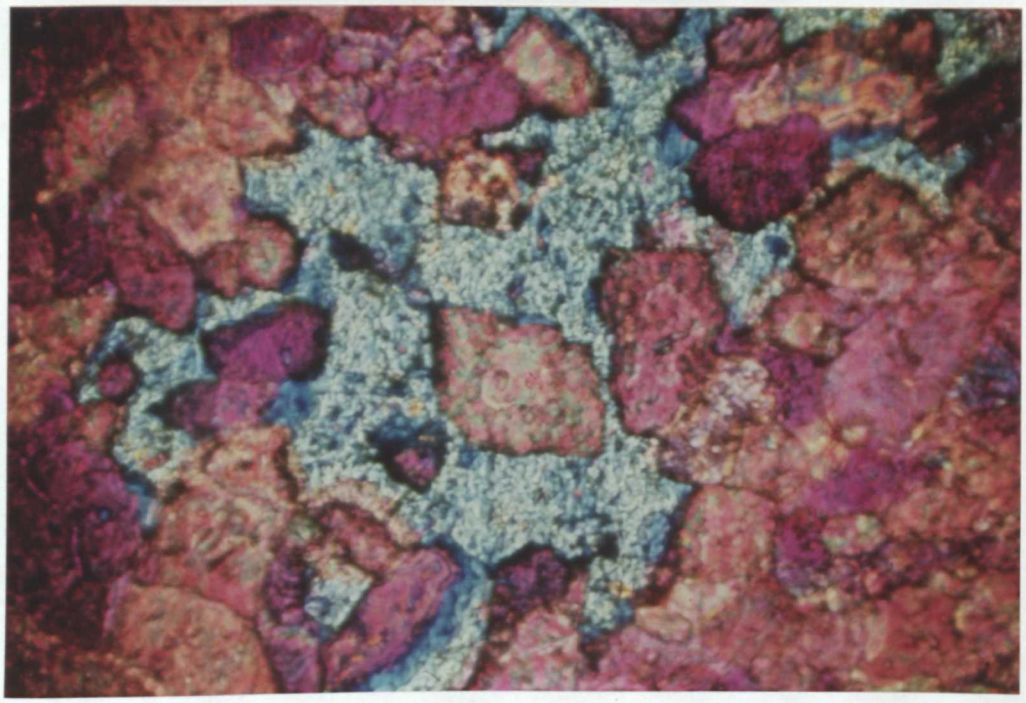
Overtoun Burn, near Dumbarton.

diameter. Crystal-size both under and over this range, however, still occur.

The crystals of this microfacies are found to be of two different origins. They are derived partly from calcitization of the original dolomitic sediment, and partly through segregation of an original calcite disseminated within an argillaceous sediment. The resulting crystals in both cases are of nearly the same composition as indicated by electron microprobe analysis, which shows that they are composed almost exclusively of calcite (cf. Tables 6.18 and 6.19, 6.22-24). Electron microprobe analyses of the original argillaceous sediment are shown in Table 6.17. Gypsum patches (Plate 3.10) of various sizes are of common occurrence, especially in the part derived by calcitization of the original dolomitic sediment.

The secondary origin of Microfacies C is inferred from its fabric and the ubiquity of the original sediment remnants. Its proposed probable mode of formation models are shown in Figs. 3.2-4.

Those fabrics which originated by replacement of dolomite occur in both stratified and nodular carbonate beds Figs. 3.6-12, whereas those resulting from displacement of argillaceous material occur in the beds considered pseudobrecciated. These beds are now composed of pure carbonate , represented by patches of the newly formed crystals in an argillaceous matrix. Read (in Francis,/



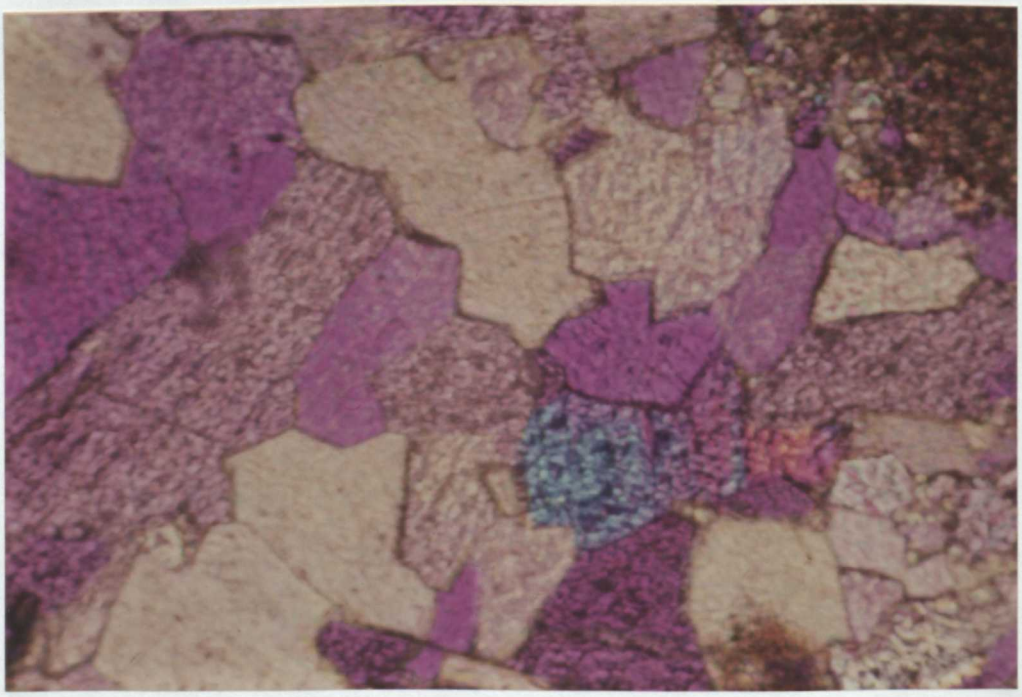


Plate 3.10

Upper: Microphotograph showing gypsum (bluish) occurrence in Microfacies C. Under crossed nicols. Mag. 40X. Overtoun Burn, near Dumbarton.

Lower: As above. Overtoun Burn, near Dumbarton.

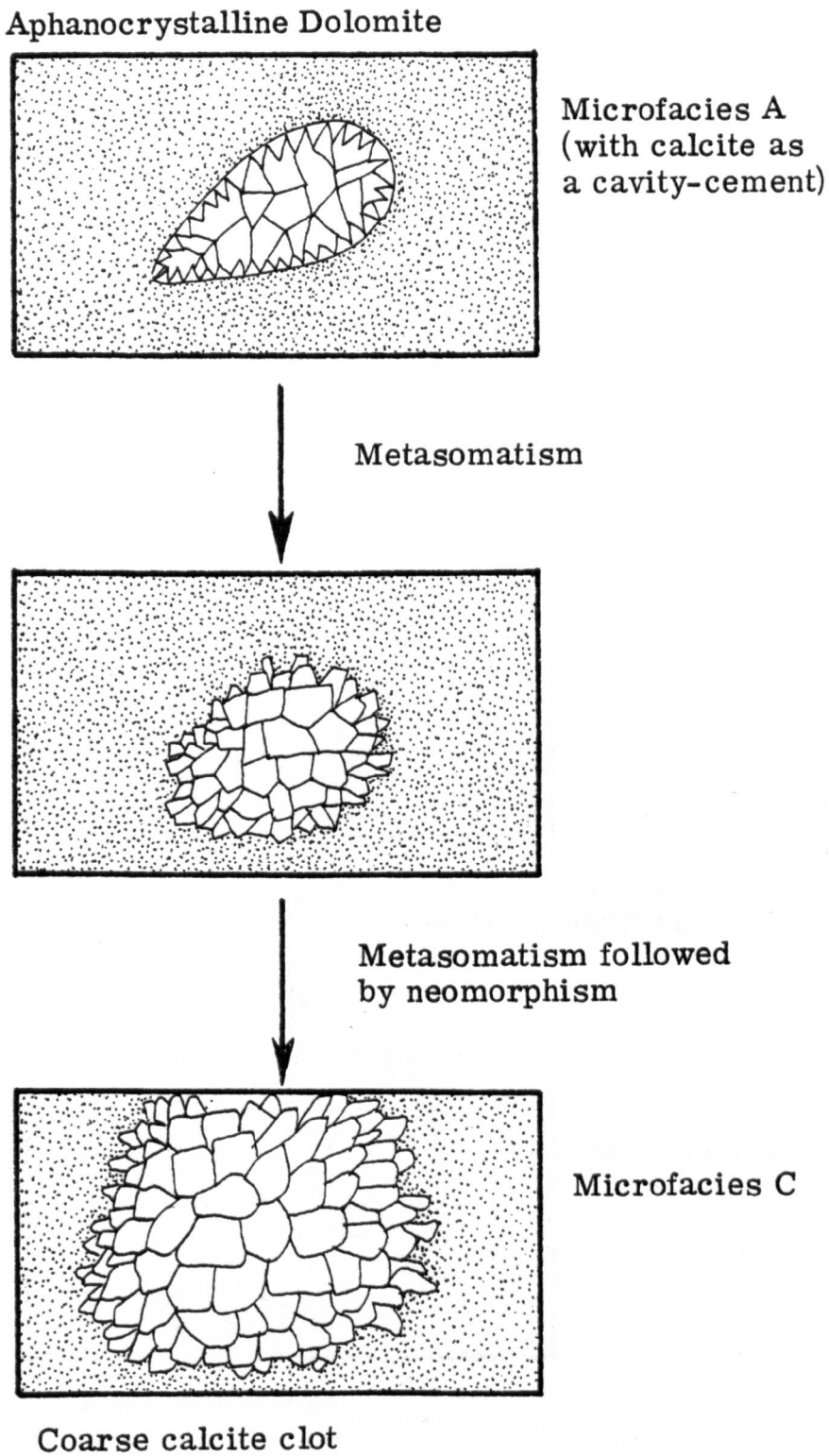


Fig. 3.2 : Enlargement of cavity-cement in formation of Microfacies C from Microfacies A. Not to scale.

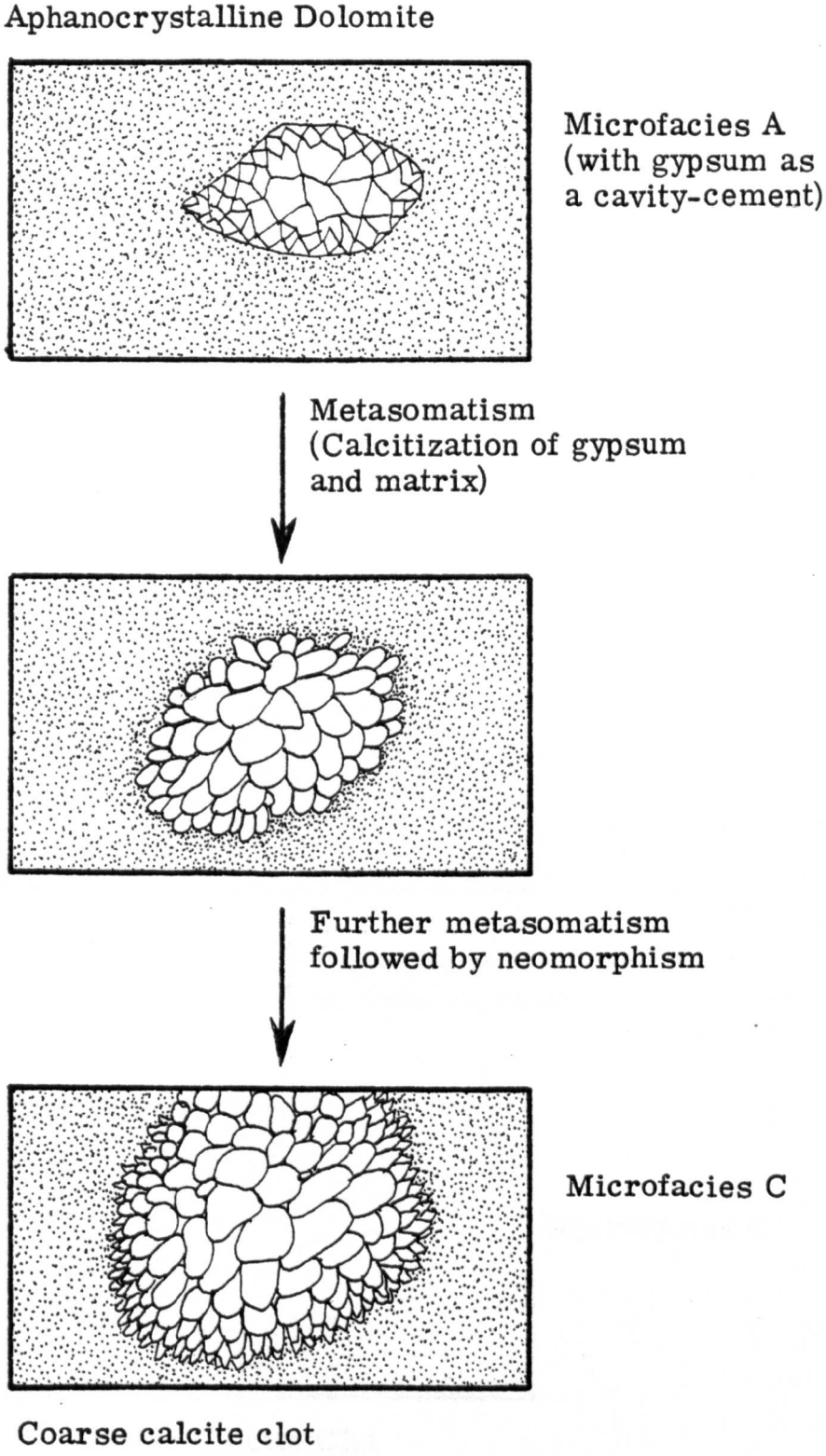


Fig. 3. 3. : Calcitization of gypsum and matrix in the formation of Microfacies C from Microfacies A. Not to scale.

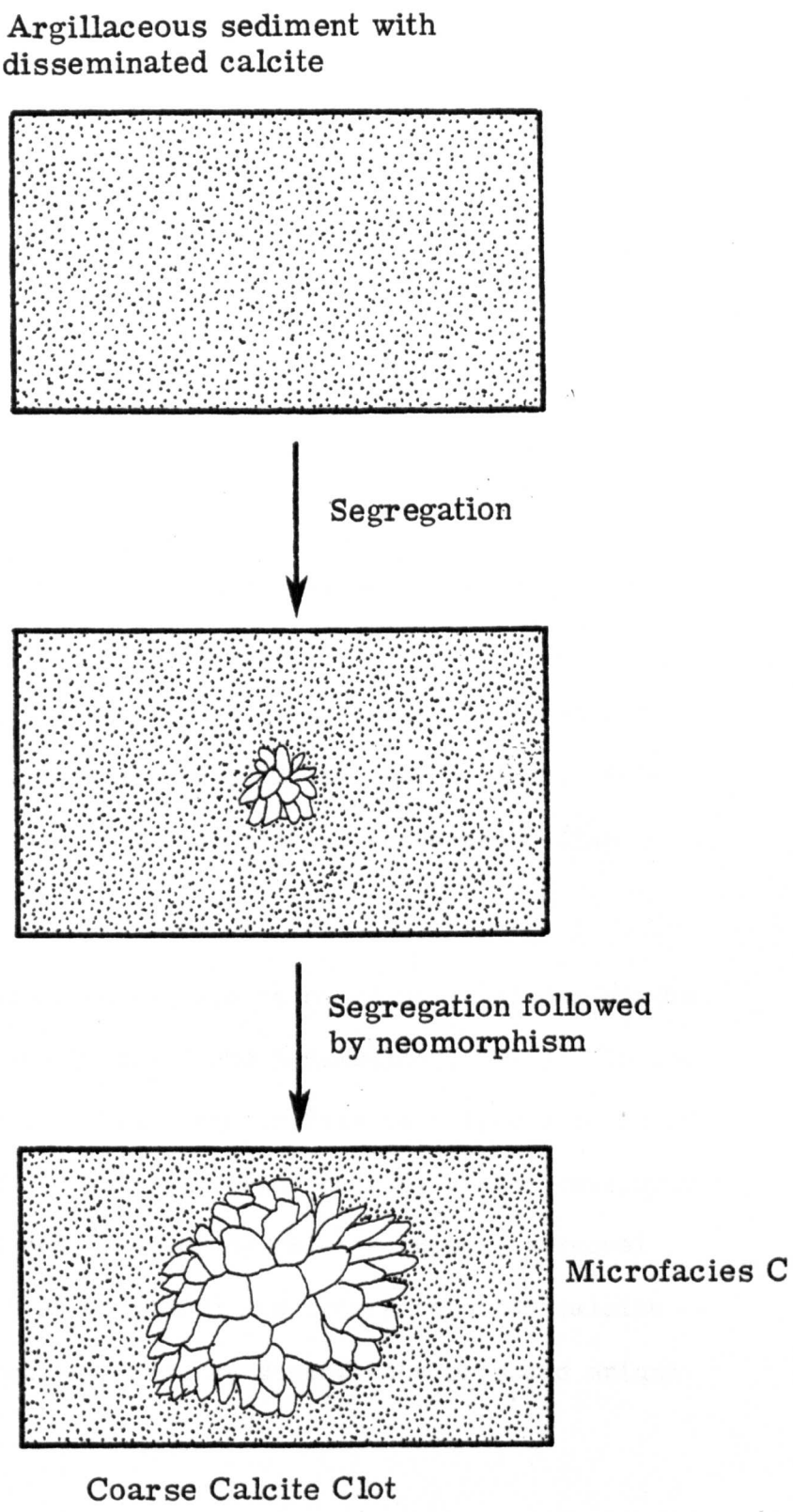


Fig. 3.4 : Stages of formation of Microfacies C in Argillaceous sediment. Not to scale

Francis, et al, 1970) described these beds in a similar manner. This microfacies is commonly of less occurrence and form approximately between 2 and 14 percent of the carbonates of the Ballagan Formation.

4. Chevron Bed

In addition to the three microfacies described above, there is a peculiar bed where chevron-structure is of common occurrence. The material forming this structure is presently composed predominantly of calcite (see analysis MG 105, Table 6.3A). This type of bed is seen only in the section of Auchenreoch Glen (Grid Ref. 420 773).

Such distinctive structure was found to be developed by the growth of halite grains (Wardlaw and Schwerdtner, 1966). In the current investigation, however, the calcite is believed to be of a replacement origin possibly after halite, as the development of this structure is not favoured by calcite (Bluck, personal communication). West et al (1968) and others reported calcite pseudomorphs after halite, this may support the proposed origin of calcite.

3.3 /

3.3 Distribution of Microfacies

The distribution of the major microfacies in the individual exposures are shown in Figs. 3.6-12. It is clear from such frequency distribution that the microfacies proportions are similar in most exposures. This indicates that the controlling factors over their development have been operative in the same manner and on a similar scale everywhere, throughout the history of these rocks.

There is no apparent relationship between the development of the microfacies and the disposition of the clastic rocks. The reason as to why the occurrence of the chevron- bed is confined to the section of Auchenreoch Glen is not clear, but it could be a localized phenomenon. However, this bed not being seen in other sections, should not rule out the possibility of its wider occurrence.

3.4 Diagenesis

The analysis of fabrics and their paragenesis has been difficult in these fine grained rocks. However, a diagenetic sequence has been proposed.

It is believed that the bulk of the present fabrics are most likely secondary in origin. Therefore, the cause of the microfacies variation is primarily sought in diagenesis.

Microscopic/

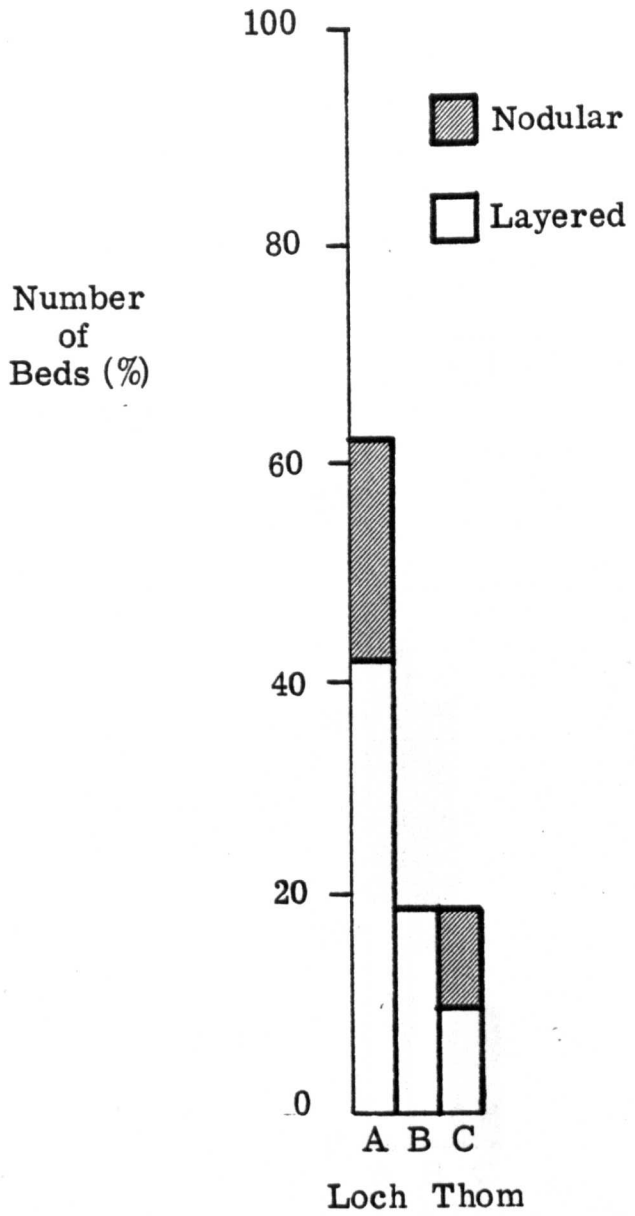


Fig3.6 : Carbonate Microfacies Distribution - Loch Thom

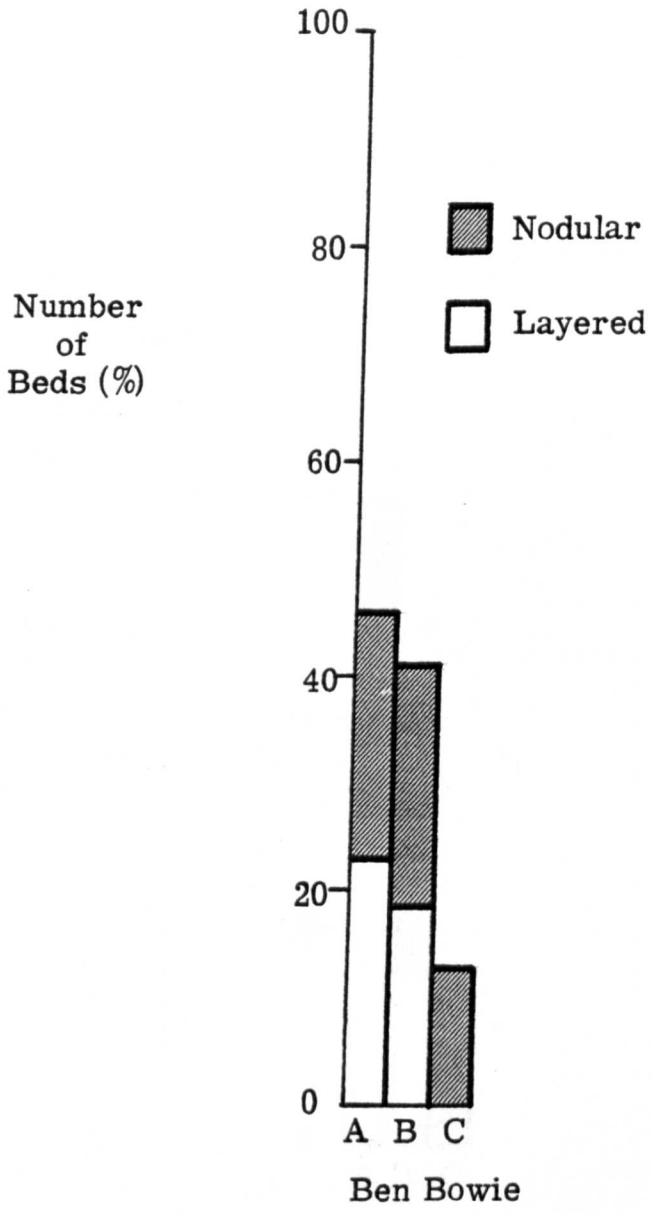


Fig.3.7: Carbonate Microfacies Distribution - Helensburgh

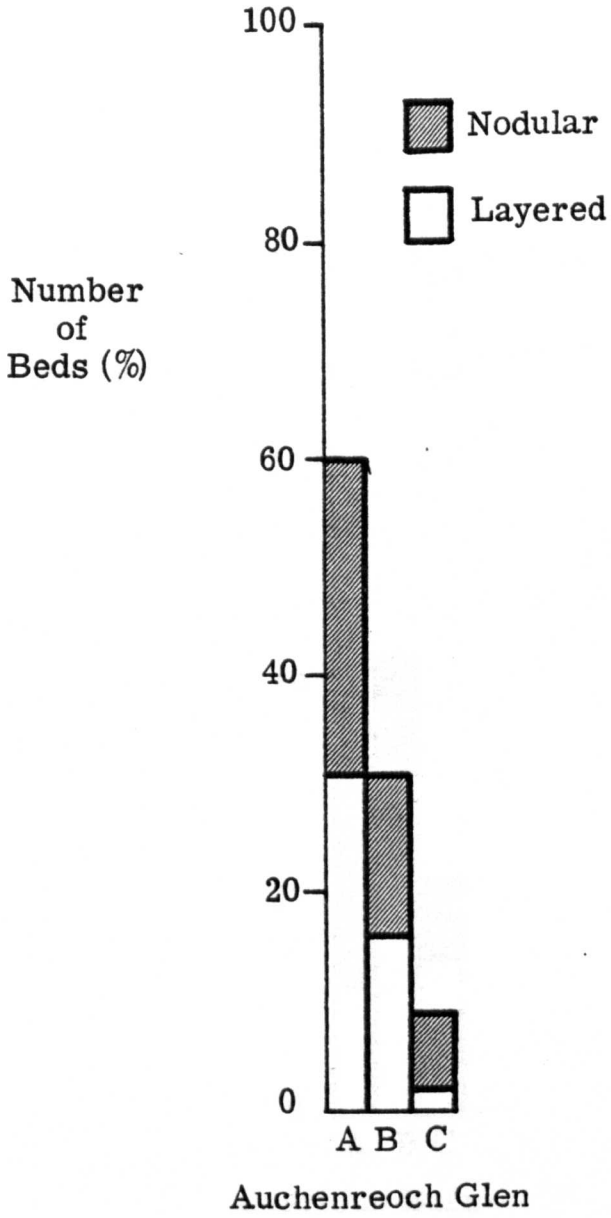


Fig. 3.8 : Carbonate Microfacies Distribution - Auchenreoch Glen

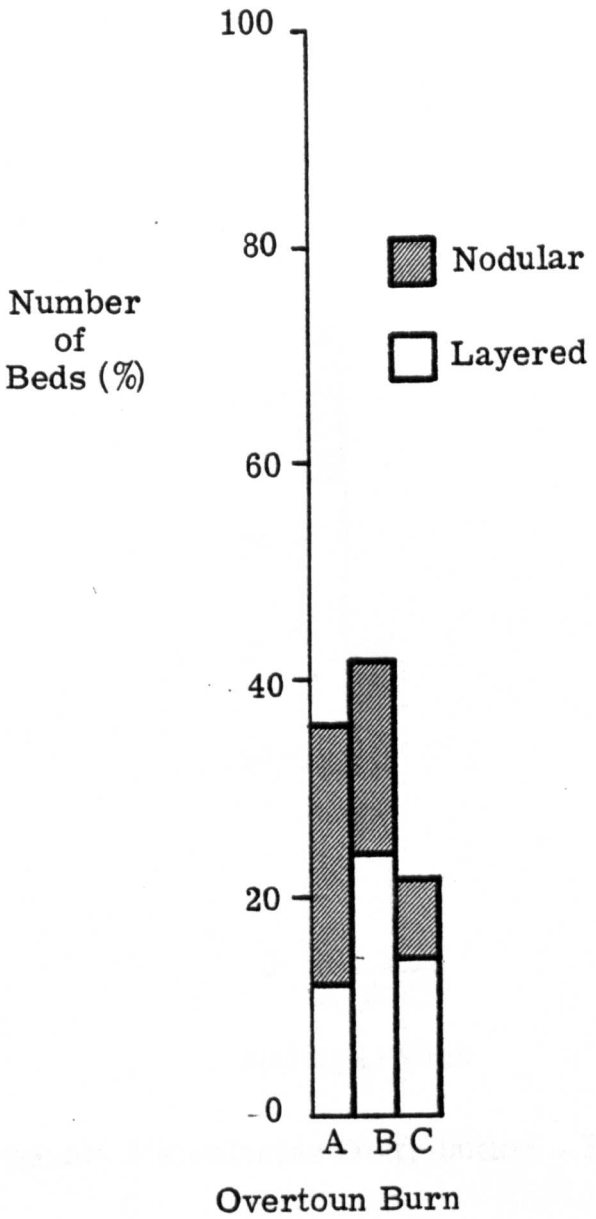


Fig.3.9: Carbonate Microfacies Distribution - Overtoun Burn

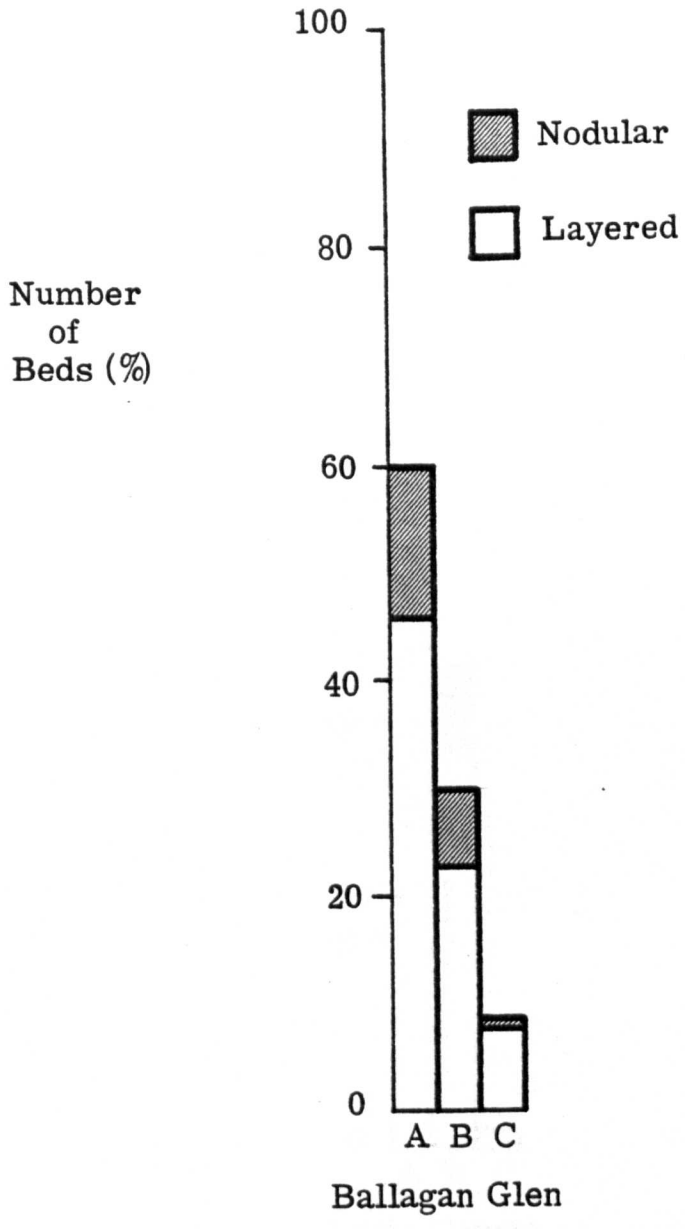


Fig.3.10: Carbonate Microfacies Distribution - Ballagan Glen

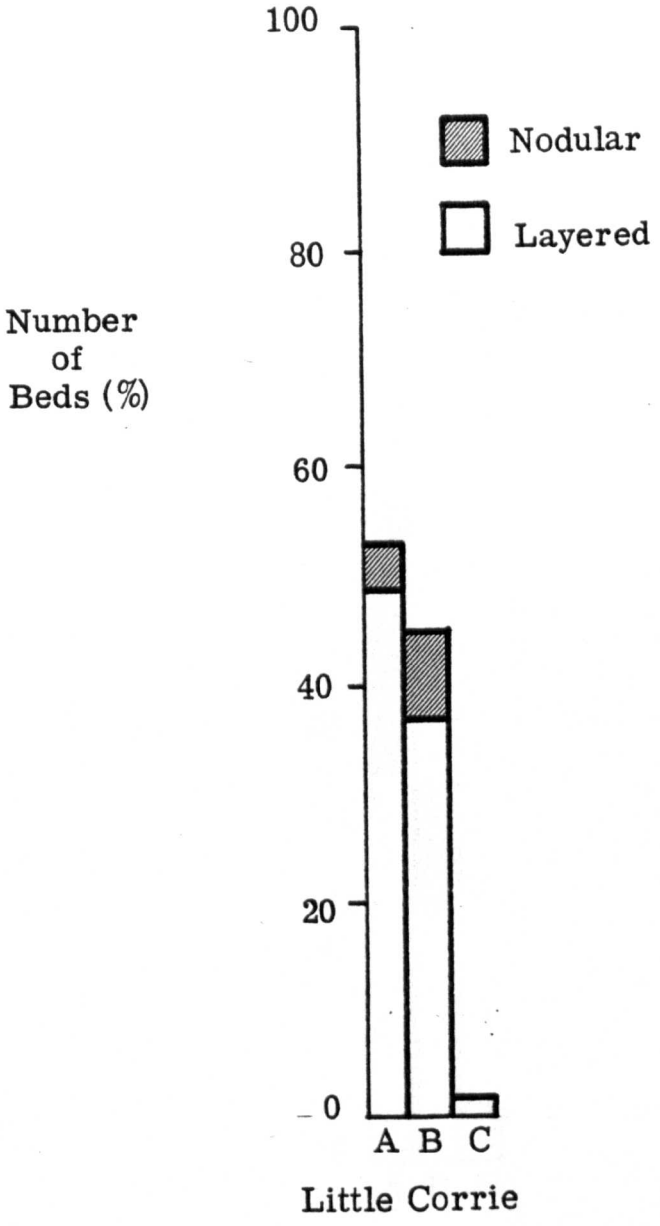


Fig.3.11: Carbonate Microfacies Distribution - Little Corrie

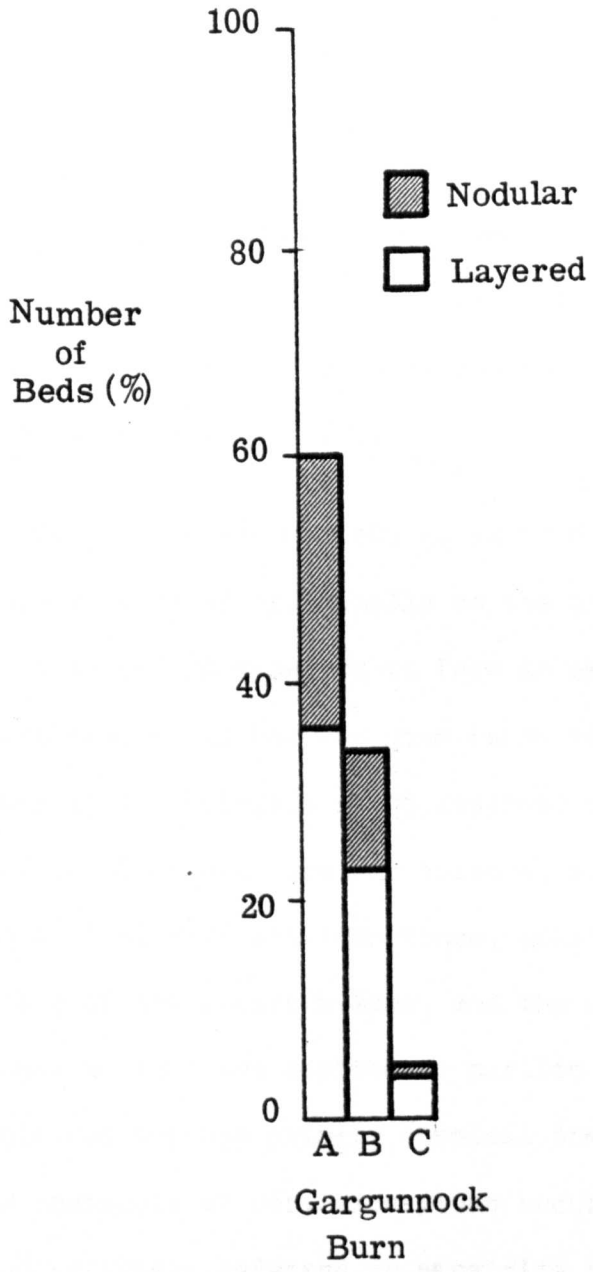


Fig. 3. 12: Carbonate Microfacies Distribution - Gargunnock Burn, Gargunnock.

Microscopic investigation of the carbonates shows that they have undergone differential diagenesis, namely, at present they range from their original fabric being virtually unaffected (Microfacies A, Plate 3.1) to almost complete obliteration of such primary fabric diagenetically. The result is the obvious development of new microfabrics (Microfacies B and C, Plates 3.8 and 3.9 respectively). These newly formed microfacies differ considerably from their precursor in terms of composition and crystal characteristics, especially Microfacies C.

Microfacies A, however, as assumed above, is of primary origin. This assumption is based principally on the grounds that no fabric finer than this can be expected to form in sedimentary carbonate rocks. Furthermore, it has not been found replacing other fabrics. Indeed it is obviously being replaced by other fabrics. Post-depositional changes are not evident, but if any took place they must have been of insignificant importance, apart from the development and filling of the cavity system, and the veinlets. It is, therefore, suggested that the carbonate portion of this microfacies originated through primary chemical precipitation. This type of rock is obviously of very widespread occurrence in the geologic record being variously referred to as calcite mudstone; calcilutite; and micrite limestone.

Microfacies/

Microfacies A is thought to have been the parent rock of both Microfacies B and C. Three major diagenetic processes are believed to be involved during the history of these replacive and displacive microfacies developments. These processes are "neomorphism", "metasomatism" and "segregation". Microfacies B is considered to be the product of neomorphism, whereas Microfacies C has been formed by metasomatism when replacing dolomite. When its development occurs in terrigenous material, the process of segregation, namely, displacement of the enclosing material, was responsible. The coarser crystals in Microfacies C are likely to have replaced finer crystals through the process of neomorphism. Therefore, it is possible to conclude that Microfacies C is the product of metasomatism, segregation and neomorphism.

3.5 Neomorphism

Neomorphism is a term proposed by Folk (1965) to describe the products of both inversion and recrystallization processes. It was defined as "All transformations between one mineral and itself or a polymorph whether inversion or recrystallization, whether the new crystals are larger or smaller or simply differ in shape from the previous ones. It does not include simple pore-space filling; older crystals must have gradually been consumed, and their place simultaneously occupied by new crystals of the same mineral or a polymorph, i.e. it is a special case of replacement in/

in the solid state, with or without interstitial liquid films, and with composition essentially constant," Folk (1965, p.21).

Bathurst (1971) expressed his objection to the part of its definition concerning the "solid-state" and called it an unfortunate use by Folk because it is widely accepted that dry, solid-state processes are insignificant in carbonate diagenesis, as the environment is inevitably a wet one.

The effect of neomorphism can be patchy as well as pervasive. The resultant fabric of the process can be finer; degrading and coarser; aggrading. Countless cases of both products have been frequently reported in the literature. Reference in this respect should be made to Dixon (in Dixon and Vaughan, 1911); Lindgreen, 1925; Wood 1941; Beales 1956; Bathurst 1958, 1959; Banerjee 1959; Folk 1959, 1965; Maxwell 1961; Schwarzacher 1961; Stauffer 1962; Wardlaw 1962; Orme and Brown 1963; Friedman 1964, 1966; Demirmen and Harbaugh 1965, Schmidt 1965; Braithwaite 1966; Evamy 1967; Oldershaw 1969; Whitcombe 1970; Wolfe 1970; Land and Moore 1980; and many others.

The change in the fabric of Microfacies A is obviously of a gradational nature as it can be seen being altered gradually from its assumed original state through stages in neomorphism, which resulted in the formation of a relatively wide crystal size range from about 5 microns up to nearly 30 microns in diameter, of the proposed/

proposed Microfacies B (cf. Plates 3.1, 3.7 and 3.8).

It warrants emphasizing that in some instances the boundary between the original and the secondary fabrics is actually an arbitrary one, and it was extremely difficult to determine to which of the designated microfacies, such cases should be assigned. Such difficulty was experienced where neomorphism does not seem to be very advanced (cf. Plates 3.1, 3.7 and 3.8).

The secondary origin of Microfacies B is inferred from the gradational boundary with Microfacies A and the inclusion of facies A in the general fabric of B. Where the development of Microfacies B is very advanced, that is, the obliteration of the original fabric is complete, it could be mistaken for an original fabric.

The neomorphic process is believed to have involved the solution of the smallest, supersoluble crystals and redeposition on the larger more stable crystals (Bathurst, 1958, 1959; Stauffer 1962; Folk 1965; Braithwaite 1966; and others). This belief, however, is based purely on the assumption that the more advanced, that is coarsest, Microfacies B fabric has been developed by the continuation in the solution - redeposition pattern as long as the newly formed crystals have not reached a certain stage of stability beyond which the process could no longer proceed (Orme and Brown 1963).

A/

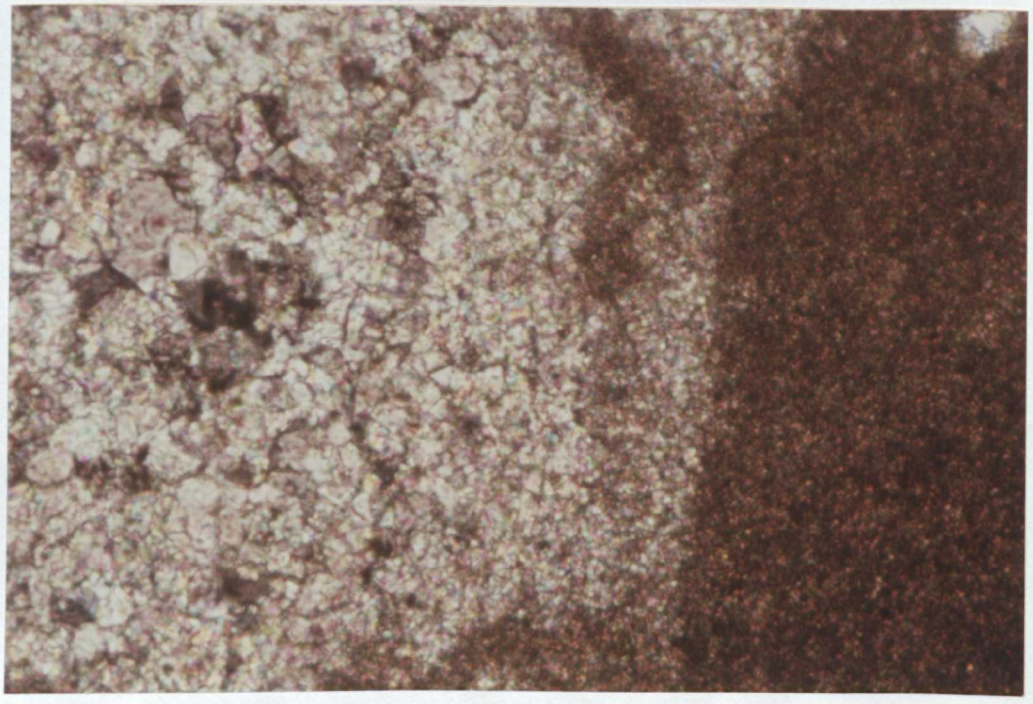
A large number of workers in the field of carbonate rocks reported the occurrence of microspar (cf Folk, 1965, p.37 and Bathurst, 1971, p.546) on a very large scale through aggrading neomorphic process (Dixon, in Dixon and Vaughan 1911; Bathurst 1958, 1959; Friedman 1964, 1966; Demirmen and Harbaugh, 1965; and Folk, 1965. Wardlaw (1962) reported microspar that was produced during degrading neomorphism of calcarenites.

Careful study of the newly formed fabric may prove that the gradational nature in its crystal size is possibly a consequence of multi-stage neomorphism. Especially where the produced crystals exceed the 15 microns limit in diameter, the author believes, as mentioned above, that the process of solution and redeposition was not confined to the primary crystals but has obviously involved the new crystals in part. Thus there is a strong possibility that by the time the present stage of neomorphism has been achieved, all crystals of the primary origin were eliminated and their place is taken by neomorphic crystals. The multi-stage neomorphism suggested can be possibly evidenced by the relative homogeneity of crystals beyond the 15 microns limit, in some instances, in a given thin section, it also can be enhanced by the gradational nature of the boundary between the fabric's consecutive crystal grades. Orme and Brown (1963) believed that more than one stage of neomorphism was possible. A probable pattern for neomorphism is proposed in Fig. 3.1.

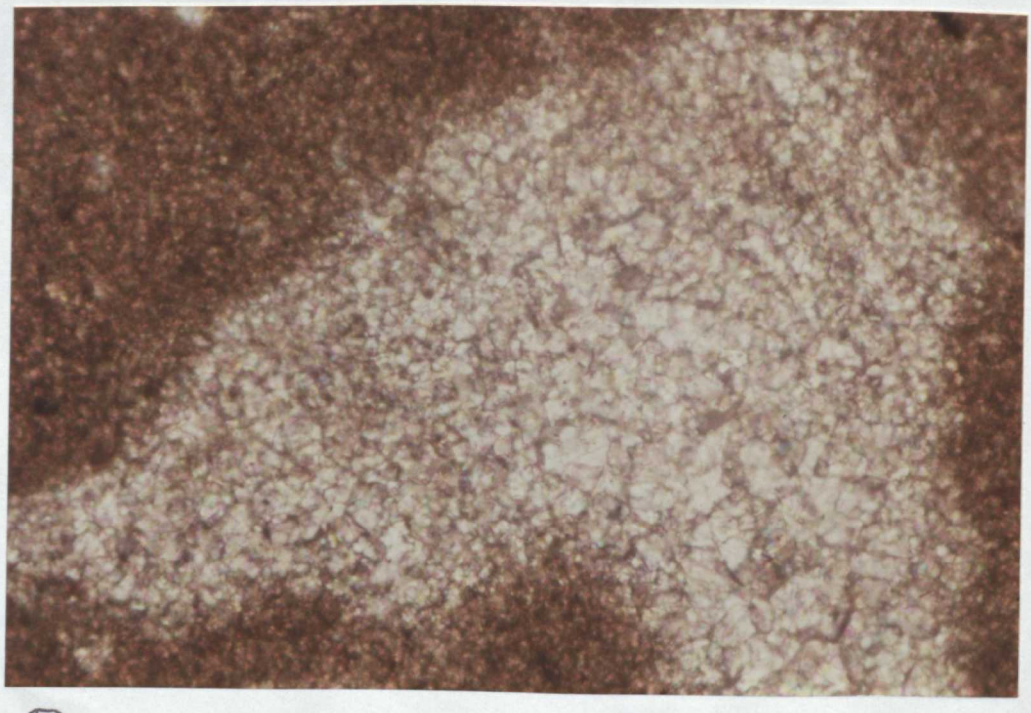
The/

The neomorphic crystals generally become clearer as they become larger. This phenomenon is considered to be the result of impurity expulsion by the new crystals, presumably gradual extrusion as such has accompanied the stages of neomorphism proposed above (cf. electron microprobe analyses, Tables 6.9 and 6.14). Dixon (in Dixon and Vaughan, 1911) reported the phenomenon of impurity extrusion and believed that this impurity was driven into the unaffected portions of the matrix. Cases from turbid to almost inclusion free crystals are documented. Nearly in every case, the impurity (clay) is believed to have partly concentrated in areas at the intercrystalline boundaries as evidenced by their relative darkness as well as electron microprobe analysis (Table 6.12). These concentrations, however, may be considered responsible for hindering further neomorphism in some cases, especially where substantial amounts of clay are present. Since clay is the major constituent of the impurity, neomorphic changes are expected to depend on it to a certain extent. Bauch (1968) found that clay mineral content in excess of 2 percent may inhibit this process.

Relatively coarser mosaics, in which crystal size reached up to nearly 150 microns in the longest diameter (pseudospar of Folk, 1965), are occasionally common (Plates 3.11 and 3.12). This is likely to have been produced by still more stages of neomorphism, that is more solution and redeposition (Beales, 1956). But it is equally likely that these clots are partly cavity cement, which could/



A



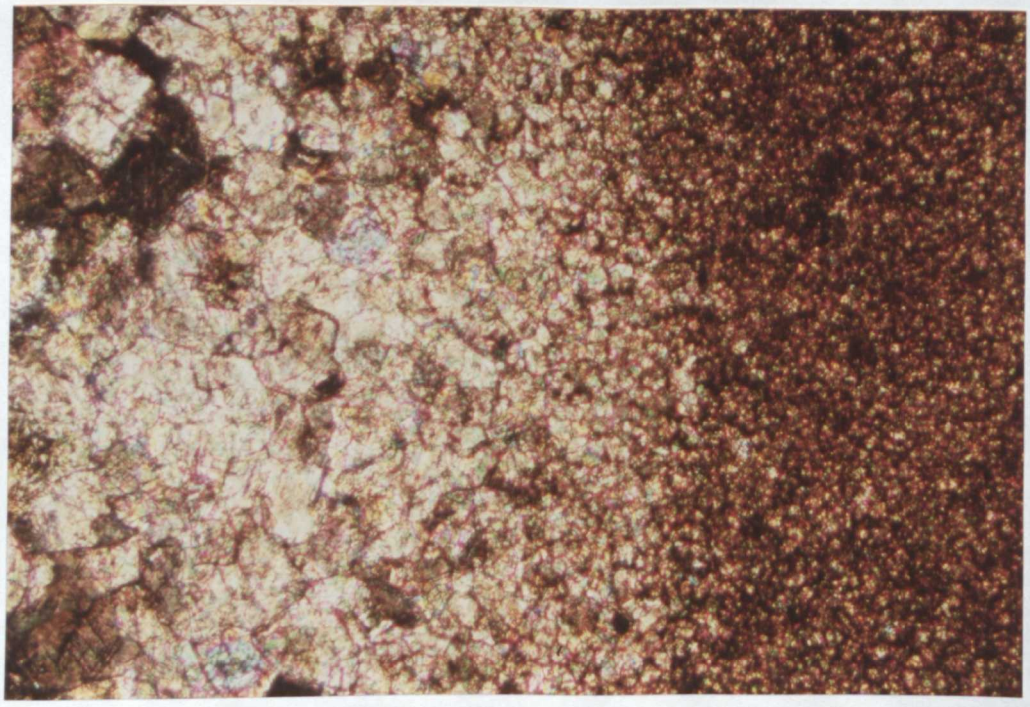
B

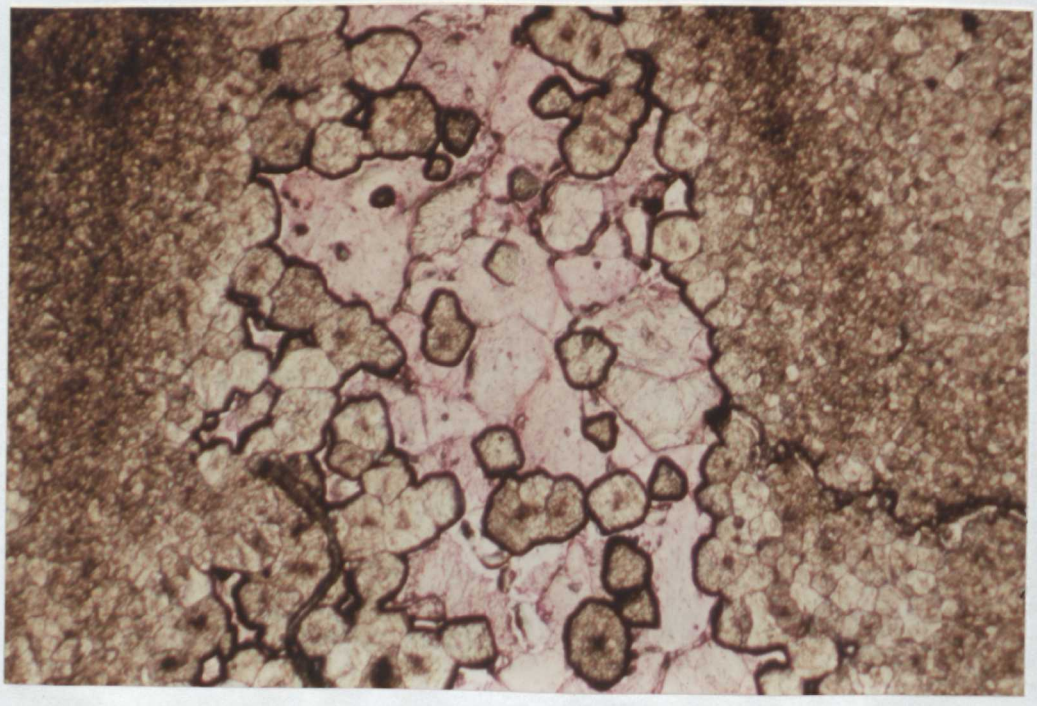
Plate 3.11

Microphotographs showing neomorphic patches with gradational crystal-size. Under crossed nicols. Mag. 40X.

A. Overtoun Burn, near Dumbarton.

B. Ballagan Glen, near Strathblane.





- Plate 3.12

- Upper: Microphotograph showing secondary mosaic with gradational crystal-size. Under crossed nicols. Mag. 40X.

Ben Bowie, near Helensburgh.

- Lower: Microphotograph showing the occurrence of dolomite rhombs in a calcite mosaic. Stained with Alizarin Red-S. Mag. 10X.

Overtoun Burn, near Dumbarton.

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could have been either primary dolomite or replacive after calcite or gypsum. Dolomite is found replacing gypsum in the Tunnel section, near Dumbarton (Bluck, personal communication). These assumptions are, however, rather difficult to prove or disprove, simply because presently these clots comprise only dolomite crystals except one case where dolomite rhombs are found floating in a calcite clot (Plate 3.11).

Folk (1965) believes that pseudospar can be produced by neomorphism. Because there are no replaced minerals present and the lack of definite margin, an important distinguishing feature between neomorphic clots and cavity cement (cf. Plates 3.6 and 3.11), a neomorphic origin for these clots is favoured. This type of clot is widely reported in the literature, and in some cases has been called pseudobreccia. Dixon (in Dixon and Vaughan, 1911); Wood (1941); Bathurst (1958, 1959); Stauffer (1962); and many others.

3.6 Metasomatism

Metasomatism was defined as "an essentially simultaneous, molecular process of solution and deposition by which, in the presence of fluid phase one mineral is changed to another of differing chemical composition, "Lindgren (1925, p. 247-248). Also defined as "diagenetic metasomatism involves introduction of materials from without, leading to replacement. "Bissell and Chilingar (1967, p.161). One of its definitions in the Dictionary of/

of Geological Terms, American Geological Institute is "replacement' the process of practically simultaneous capillary solution and deposition by which a new mineral of partly or wholly differing chemical composition may grow in the body of an old mineral or mineral aggregate".

Metasomatism is a phenomenon of a very wide spread occurrence in the carbonate rocks throughout the geologic record. This process is reported mainly in the form of dolomitization and calcitization, which both take place in ancient as well as recent sediments. In some cases, terrigenous sediments are involved in this process, namely dolomitization and calcitization, presumably on relatively smaller scale.

The present investigation of the carbonate intervals in the Ballagan Formation indicates that calcitization of dolomite has most probably taken place. "Calcitization" is used to describe the replacement process of material by calcite, whether dolomite or otherwise, in support of Smit and Sweet (1969) for their call upon geologists to give up the use of the term "dedolomitization", to avoid the ambiguity created, should its use be maintained, especially if applied to dolomite replacement by minerals other than calcite, which is a common phenomenon, this will obviously result in an avoidable misleading terminology.

The/

The characteristics of Microfacies C, as previously described are indicative of its secondary origin. The evidence for such indication, possibly lies in the fact that sparry calcite, of such characteristics, has not been reported as forming a rock on its own, in the form of primary chemical precipitate. Also the form in which it is occurring, namely, mostly as coarse calcite clots, is a likely further proof for this origin. Therefore, it is inferred that Microfacies C is evidently secondary in origin, even in the absence of the remnants of the original sediment, and thus, the responsible process is obviously metasomatism.

It is rather important to emphasize that the characteristics of Microfacies C, developed in both the dolomitic and argillaceous sediments, are identical in almost all aspects. Thus, in the absence of remnants of the original sediment, speculation regarding the parent rock, may result in an erroneous interpretation in this respect.

The occurrence of gypsum in Microfacies C (Plate 3.10), in such form, may indicate that it had played a role, possibly an important one, in bringing about calcitization. Gypsum may have been present as a primary sediment and/or cavity-cement, then replaced by calcite. The presence of these two gypsum types and their calcitization are documented in Plates 3.4 and 3.6. Reporting of calcite after gypsum (West et al, 1968) in similar sediments, may be considered as further supporting evidence for the proposed replacement/

replacement. Calcitization, however, was not confined to the gypsum, but has evidently affected the dolomite as well.

3.7 Replacement of Dolomite

Several carbonate intervals originally constituted mainly of aphanocrystalline dolomite with certain amounts of argillaceous material, are found partially calcitized.

The metasomatic process is believed likely to have been triggered by some sort of changes within cavity-cement, such as calcitization of gypsum or can be merely an enlargement phenomenon of such cement, at the expense of the matrix, especially when calcite was the primary cement. Munn and Jackson (1980) believed that most of the calcitization begins around calcite-filled pores in the dolomite and suggested that calcitization of dolomite peripheral to calcite-filled pores may develop to give large, very irregular areas of calcite.

The last major filling mineral to occupy the cavities, which may have been involved in the process of metasomatism, is generally considered calcite, either of primary or replacement origin. The latter is most likely to be after gypsum as evidenced by some relics floating in the calcite mosaics. West et al.(1968) and Kocurko(1979) showed that gypsum has been replaced by calcite. Von Morlot (1848 in Shearman et al,1961)discussed the possible role of magnesium sulphate in the formation of dolomite according to his/

his equation:

$$2\ CaCO_3 + MgSO_4 \rightleftharpoons CaCO_3\ MgCO_3 + CaSO_4$$

He observed that this is a reversible reaction, and suggested that a gypsiferous solution could cause calcitization of dolomite.

In the present investigation, it is possible that calcite did not confine itself to the limits of the cavities it occupied. It has obviously spread around them at the expense of the matrix, which comprises the crypto-crystalline dolomite. The intensity of the replacement process, which may have depended to a large extent on the size of the cavity involved, has consequently resulted in the production of sparry calcite mosaics, variable in shape and size. The crystal-size within the clots, as it is always the case, increases towards the centre of these clots. In the absence of the gradation in crystal size, it would be a mistake to call them anything but cavity-cement. A possible sequence of stages in the formation of Microfacies C in dolomitic sediment is proposed in Figs. 3.2 and 3.3.

Where metasomatism was pervasive, the clay seemed to accumulate at least in part, in irregular elongate patches. The produced sparry calcite crystals seem to be almost inclusion-free. Both phenomena are evidenced by electron microprobe analysis, Tables 6.25 and 6.20, 6.21 respectively. The other possibility of the calcitization process is that described by Shearman et al (1961) who believed that in rocks where centripetal replacement can be demonstrated/

demonstrated to have taken place, the replacement was by larger calcite crystals which poikilitically enclosed the dolomite. This type of calcitization they thought has only affected rocks, which were essentially dolomite, and which consisted of a highly packed aggregate of dolomite crystals.

De Groot (1967) studied experimentally the calcite replacement of dolomite and concluded that the following conditions are necessary for effective calcitization :

1 - A high rate of water flow to remove Mg ions formed thus keeping the Ca/Mg ratio of the water constantly high.

2 - A carbon dioxide partial pressure considerably lower than 0.5 atmosphere.

3 - Temperatures not higher than 50^{o} C.

Clark (1980) reported two types of calcite after dolomite, one of which was described as coarsely crystalline and considered to be formed when large calcite crystals poikilitically replaced large numbers of dolomite crystals, and conditions proposed by de Groot (1967) were thought responsible for the calcitization.

There is, however, a good reason to adopt and consider the conclusions of both Shearman et al (1961) and Clark (1980) for the belief that calcitization has taken place in the rocks under study, since the characteristics of both the original sediment and its replacement are similar to those described by these authors.

Schmidt/

Schmidt (1965) attributed calcitization to deep surface weathering evidenced by an increase in the intensity of the process as an unconformity is reached. Evamy (1967) arrived at similar conclusion, when he suggested that calcite after dolomite, in the subsurface, should be considered as evidence of former emergence.

In the calcitization of dolomite, neomorphism is assumed to have operated with metasomatism, possibly simultaneously in some instances. This phenomenon is believed to have proceeded by some metasomatic crystals, presumably more stable, increasing in size at the expense of those less stable but of the same origin. The evidence lies in the development of gradational crystal size, which is obviously increasing towards the centres of the clots. They are called neomorphic clots, on the basis that neomorphism is considered responsible for their present state. This process, as pointed out by Orme and Brown (1963), may have acted in more than one stage, as proposed in Figures 3.2 and 3.3.

3.8 Displacement of Clay

The layers with brecciated appearance in the field, are found to be comprised of clay material, with disseminated calcite. The evidence is provided by electron microprobe analysis (Table 6.16, Fig. 6.30). Presently, some of this calcite is found concentrated in mosaics of various sizes. Their electron microprobe analyses are given in Table 6.17.

The/

The occurrence of these coarse calcite clots is assumed to have resulted by the segregation of this mineral from the original sediment. This obviously has caused the displacement of clay by calcite. The clots do not contain clay in appreciable amounts, especially when the process seems well advanced, as indicated by the size of the clot. Thus, it can be concluded that the segregation has been a slow process. Had the process been rapid, entrapment of some clay in the newly formed crystals could be expected. However, the characteristics of Microfacies C, produced by the segregation of calcite in the argillaceous sediment, are in no way different from those produced by the metasomatism in the dolomitic sediments.

The absence of dolomite in some, if not all, of these layers, is indicated by the good positive correlation of MgO with Al_2O_3 (Fig. 6.29). Further proof is provided by the results of the computation of mineral proportions from chemical analyses, see for example analyses MG52 and MG77 in Tables 6.2A and 6.4A respectively.

Although dolomite is a likely source for these calcite clots, essentially clay through its calcitization, its absence in these layers is an evidence sufficient to exclude it from being a source. The possibility of clay being replaced by calcite may be difficult to explain. Therefore, the only alternative left, may be the assumed segregation of/

of the calcite originally present in the sediment, as the most obvious process responsible for the formation of these calcite clots. The mechanism by which the process has operated is not clear. A likely sequence of Microfacies C development is proposed in Figs. 3.2-4.

These layers are presumably those described by Read (in Francis et al, 1970) as having a brecciated appearance with fragments of relatively pure carbonate in a more aregillaceous matrix.

Although no proof can be offered, it is suggested that there is a probability that neomorphism; metasomatism; and segregation of calcite have acted simultaneously, with the development of the cavity-system in the original sediment, namely, Microfacies A. Therefore, there is a possibility that several different sets of factors have influenced the original sediment, as indicated by the difference in the replaced material and the product of these processes. Some of these factors are likely to have produced the cavity-system in Microfacies A, some were involved in the formation of the neomorphic fabric of Microfacies B, whereas others have been engaged in the development of Microfacies C. Some of these factors may be related to the original composition of the sediment involved,such as gypsum as shown by its presence in Microfacies C. Clay minerals may have played a role in the diagenesis of the original sediment.

In/

In conclusion, Microfacies A is considered as the representative of the original sediment and consequently as the parent rock for both Microfacies B and C. In terms of paragenesis, Microfacies C is perhaps the most diagenetically altered of all microfacies.

3.9 Carbonates Formation Model

A formation model is proposed in Fig.3.5 for the carbonates. It is assumed that they were formed in a restricted body of water, most likely a semi-closed lagoon. This lagoon received various amounts of terrigenous material, predominantly clay, during the development of the carbonate horizons.

It is believed that there were at least two situations in which the formation of carbonate minerals took place. One is where dolomite and calcite were likely forming simultaneously, this resulted in the development of dolomitic horizons. In another situation only calcite seemsto have formed in substantial amounts, this resulted in the development of the presently brecciated horizons.

The rate of evaporation in addition to the availability of the concerned elements are, however, suggested to be the major factors determining the formation of carbonate minerals. Thus, with high evaporation in the presence of sufficient Mg, dolomite was/

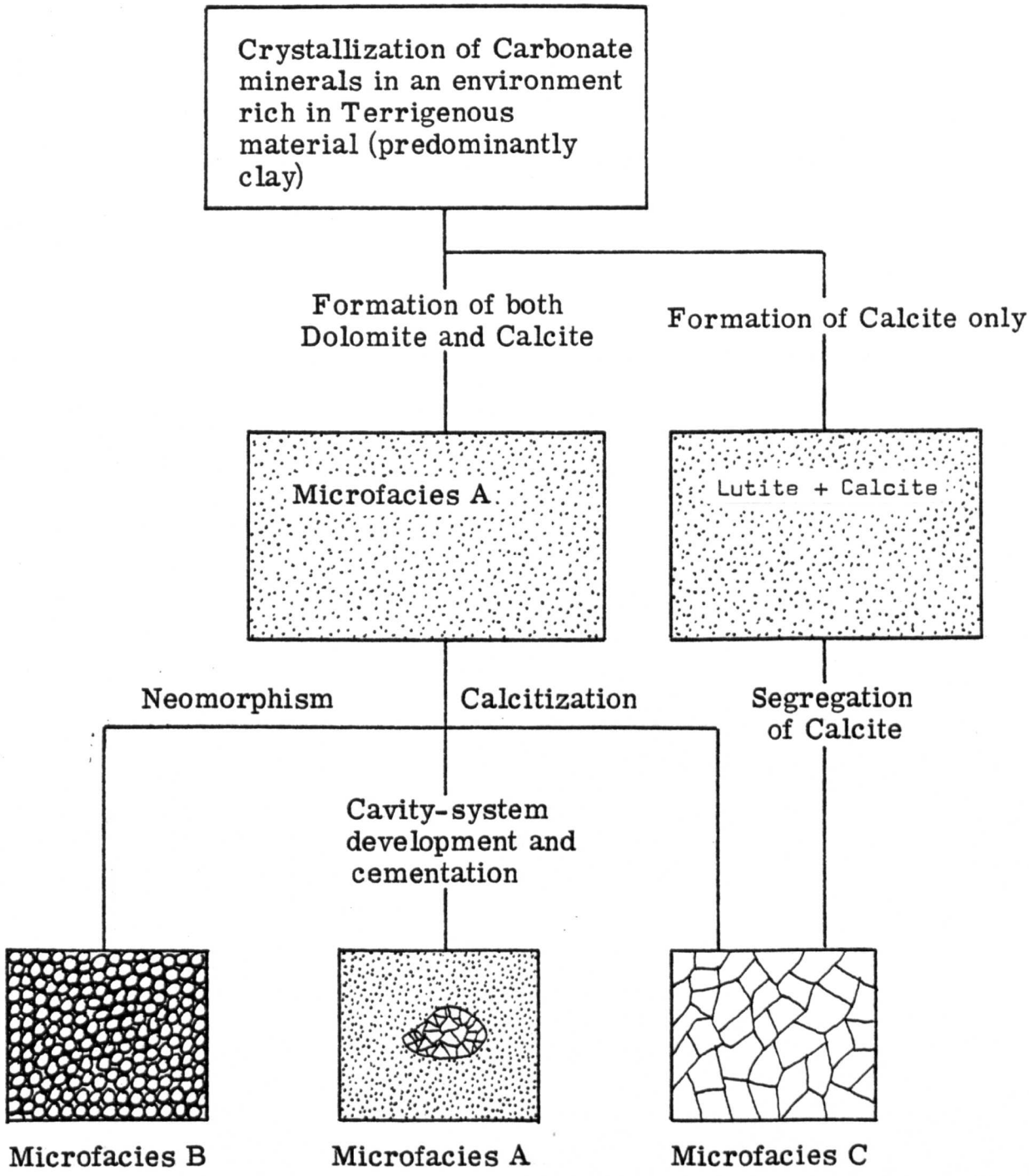


Fig. 3.5 : Proposed Model for the Formation of Carbonates in the Ballagan Formation. Not to scale.

was formed. Low evaporation coupled with scarcity of Mg resulted in formation of calcite. The resultant deposits in both cases are designated Microfacies A.

Microfacies B and C were diagenetically developed from Microfacies A, their parent rock. The first through the process of neomorphism, and the latter by calcitization and/or segregation processes. All these processes have been discussed earlier in this chapter.

CHAPTER FOUR

STRUCTURES

The carbonate beds of the Ballagan Formation contain several structures, most of which are post-depositional. These structures include: laminations; shrinkage cracks; cavity-system; and veinlets network.

4.1 Laminations

Poorly developed laminations(Plate 3.5) occur in the carbonate beds. They are uncommon in rock exposures, but more common in thin sections. Whilst it is difficult to prove an algal origin for these poorly preserved structures, they resemble,in morphology, algal laminations. Such poor preservation may indicate that they had suffered from diagenesis. Muir et al (1980) reported destruction of algal laminations which became difficult to identify in some cases. Therefore, the laminations of the present study, may be considered algal in origin and if this was the case, there is a possibility that they had developed on a relatively larger scale than they presently indicate.

4.2 Shrinkage Cracks

Wedge shaped cracks, often filled with secondary minerals, occur widely in the carbonate beds. They occur both in the laterally/

laterally persistent beds and in the nodules. Most of the cracks have a polygonal shape in plan (Plate 4.1 and 4.2), resembling the subaerial mud cracks, which occur when wet mud dries out.

The shrinkage cracks in the carbonate beds of the Ballagan Formation, however, occur all over some of the nodules surfaces, so that some would have faced downward into the underlying mud.

Matrix is not common in these cracks, however, in some instances it occurs, in the form of what appears to be a broken piece at the very top part of the crack. They are presently occupied predominantly with chemically precipitated minerals, which sometimes occur in different associations in a given crack. Calcite is the dominant fill, followed by dolomite and gypsum. Other minerals may be present but are generally rare.

Polygonal cracks occur widely in the geological record, and are often ascribed to shrinkage. Shrinkage of this kind may be due to exposure (e.g. mud cracks) or to cracking under water by reduction in volume (synaeresis).

The origin of many fossil cracks is still controversial. Some are believed to have developed subaerially, these are the most common: others subaqueously; and still others are thought to have formed under some thickness of a sediment cover.

Most/

Plate 4.1

Photographs showing shrinkage cracks in stratified carbonate beds.

Auchenreoch Glen, near Dumbarton.

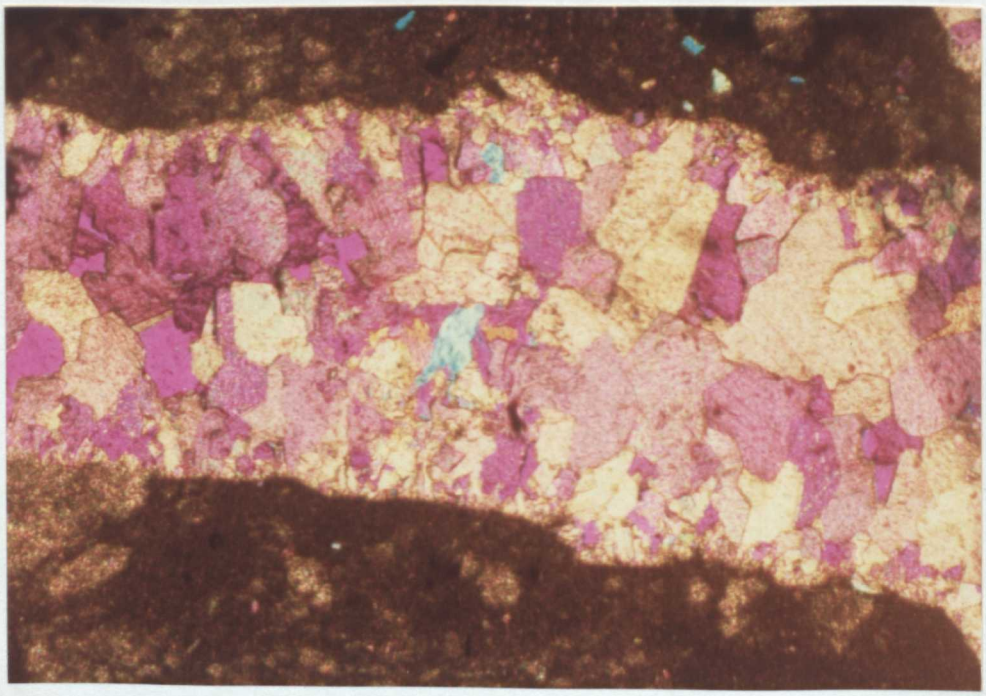


Plate 4.2

Upper: Photograph showing shrinkage cracks in a carbonate nodule. Bar is 2 cm.

Auchenreoch Glen, near Dumbarton.

Lower: Microphotograph showing a calcite veinlet. Under crossed nicols. Mag. 10X.

Overtoun Burn, near Dumbarton.

Most of the workers, however, attribute the formation of cracks, in sediment mud, to subaerial exposure. Matter (1967) believes that mud cracks almost invariably form when water-saturated muds become exposed to the air. Moore (1914), however, ascribed the development of cracks under water to ground freezing, with expansion, and later thawing, with contraction. Rich (1951) attributed the occurrence of cracks in micritic limestones and shales to subaqueous or under sediment shrinkage, in association with the expulsion of water during compaction. White (1961) used the absence of both curling at the surface and wedge shape, as an evidence for their synaeresis origin. He suggests that this type of cracks forms in clays, which appear to have been deposited in a flocculated state.

Burst (1965) produced experimentally shrinkage cracks, in clay, under subaqueous conditions. He suggests that their formation is controlled by the swelling clay mineral that affects the bulk volume changes in argillaceous sediments.

Dunbar and Rodgers (1957) object to the subaqueously origin of cracks, and they state: "They are not normally produced in the tidal zone because the interval between tides is too short to permit thorough desiccation and if they even form under standing water it is under very local and exceptional conditions that are not understood. The few instances of mud cracks alleged to have been/

been formed under water are not well substantiated and may have some other explanation "Dunbar and Rodgers (1957, p. 199).

Schwarz (1975) identified both subaerial and subaqueous cracks. The latter, he believes, is likely to be formed by variation in salinity and compaction of rapidly settled muds. The sediment was stiff enough to prevent the cover material from pressing into the cracks. Assereto and Folk (1980) used mud cracking as an evidence for subaerial exposure. Fuzesy (1980) reported the common occurrence of V-shaped cracks in limestone. These cracks were found to be filled with the surrounding argillaceous material.

Tucker (1981) attributed the origin of cracks to desiccation. The loss of water, he believes, occurs from pore-spaces between sediment grains, the loss of water contained within clay mineral lattice have caused shrinkage.

The occurrence of cracks on the under surface of many stratified carbonates in the Ballagan Formation is believed to have been developed by the same process responsible for cracks formation on the upper surface, shrinkage. Dunbar and Rodgers (1957) ascribed what they considered conspicuous shrinkage cracks on the under surface of a limestone layer, c 0.20 metre thick, to the possibility/

possibility of considerable percentage of clay or organic impurity inclusion, they suggest that shrinkage was produced by desiccation after the lake had dried up.

The cracks developed in the carbonate beds under investigation are likely to be of two different origins. Some are considered of subaerial origin as they are found containing clay sediment. Read(in Francis et al, 1970) ascribed the formation of these cracks to desiccation, also West et al (1968) attributed the development of cracks in similar sediments, to subaerial desiccation. Muir et al (1980) and many others reported stratified infilling of cracks which they believe had formed subaerially.

Other cracks in the present study are assumed to have developed under a sediment cover, as may be indicated by lack of matrix, with the exception of some broken pieces and their infill which is composed almost exclusively of chemically precipitated minerals. This assumption is offered on the basis of lack of matrix and the secondary minerals are expected to take rather a long period of time to completely cement these cracks, which may have not been allowed by the environmental conditions. The lack of matrix could be attributed to the rigidity (semi-consolidation) of the overlying sediments.

Further support for this assumption can be found in the similar cracks which developed in nodules. These nodules are believed to have formed under a sediment cover, emergence subsequent/

subsequent to their formation is unlikely. Thus, the cracks in the nodules had most likely developed under a sediment column and, therefore, such origin may be applicable at least to some of the cracks formed in the stratified beds.

4.3 Cavity System

This feature is of common occurrence in the carbonate layers presently represented by Microfacies A (Plate 3.6). They vary both in shape and size. Internal solution of the sediment is the most likely process responsible for their formation (see Bathurst, 1959; Orme and Brown, 1963; Schmidt, 1965; and Braithwaite, 1966). Other possibilities listed by Bathurst (1959) such as solution of aragonite debris; decomposition of organic tissue; and burrowing, are excluded on the grounds that, all these conditions are expected not to have existed in the carbonates of the Ballagan Formation.

Subsequent to their development, the cavities show almost all stages of filling, this ranges from complete cementation to virtually no cement. Lack of matrix in the cavities may indicate that early development of this feature did not take place. The present fill is comprised predominantly of chemically precipitated minerals, including calcite; gypsum; and possibly dolomite.

In/

In some instances two minerals are found occupying the cavity. The minor mineral is likely to be of replacement origin. This association is mainly involving gypsum and calcite, the latter is perhaps replacing gypsum. Kocurko (1979) reported the occurrence of gypsum as void-filling precipitate. He thinks it has suffered from subsequent alteration. This alteration caused much of it to undergo dissolution or replacement by calcite. This conclusion supports the proposed origin of gypsum and calcite in these rocks.

4.4 Veinlets

In the carbonates of the Ballagan Formation, veinlets are a very common feature in Microfacies B in particular.

The characteristics of this structure, such as size; shape, orientation; abundance; and composition are found to have considerable variation. Their size varies from microscopic to megascopic as it reaches up to few mm thickness in some instances. The shape is remarkably variable, irregular, branching and occasionally found in a net-like form. In addition, there are small V-shaped veinlets, especially on the periphery of some nodules. They vary in orientation generally from vertical and/or subvertical to horizontal. The carbonate layers are evidently differentially affected by veinlet development. As mentioned above, Microfacies B is severely traversed by a network of this feature in some cases. Their/

Their composition is equally variable. The filling material is found to include commonly calcite; dolomite; and gypsum. Other minerals, celestine and possibly others are less common.

The filling material generally consists of anhedral crystals which are almost always normal to the walls. The size of these crystals, which obviously increases towards the centre of the veinlet, is dependent on that of the veinlet.

4.5 Types of Veinlets

In the present study, there are three different recognizable types of veinlets, some of them are microscopic. They are sub-divided on the basis of their composition. For convenience, these will be named and referred to as follows :

1 - Single-mineral veinlets

2 - Double-mineral veinlets

3 - Treble-mineral veinlets

4.6 Single-Mineral Veinlets

This is generally the prevailing type containing calcite or dolomite or gypsum (Plate 4.2 and 3). The filling mineral is assumed most likely to be primary in origin through chemical precipitation. This assumption is based exclusively on the mode of crystal growth, which obviously displays a typical form of primary/

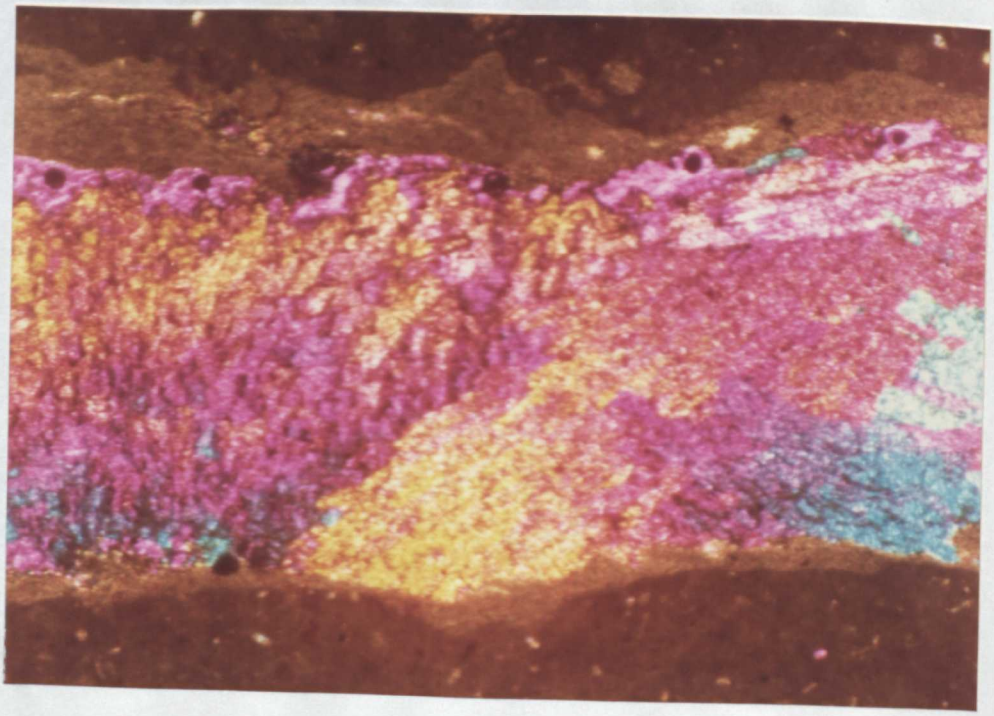


Plate 4.3

Upper: Microphotograph showing a dolomite veinlet. Under crossed nicols. Mag. 10X.

Overtoun Burn, near Dumbarton.

Lower: Microphotograph showing a gypsum veinlet. Under crossed nicols. Mag. 10X.

Auchenreoch Glen, near Dumbarton.

primary chemical precipitation in this type of structure. These crystals have grown normal to the walls, they increase in size towards the centre of the veinlet. The occupation of the veinlet by only one mineral, may be considered as a further evidence for the assumed primary origin. However, although a veinlet is monomineralic, complete replacement of a previously existing mineral cannot be ruled out.

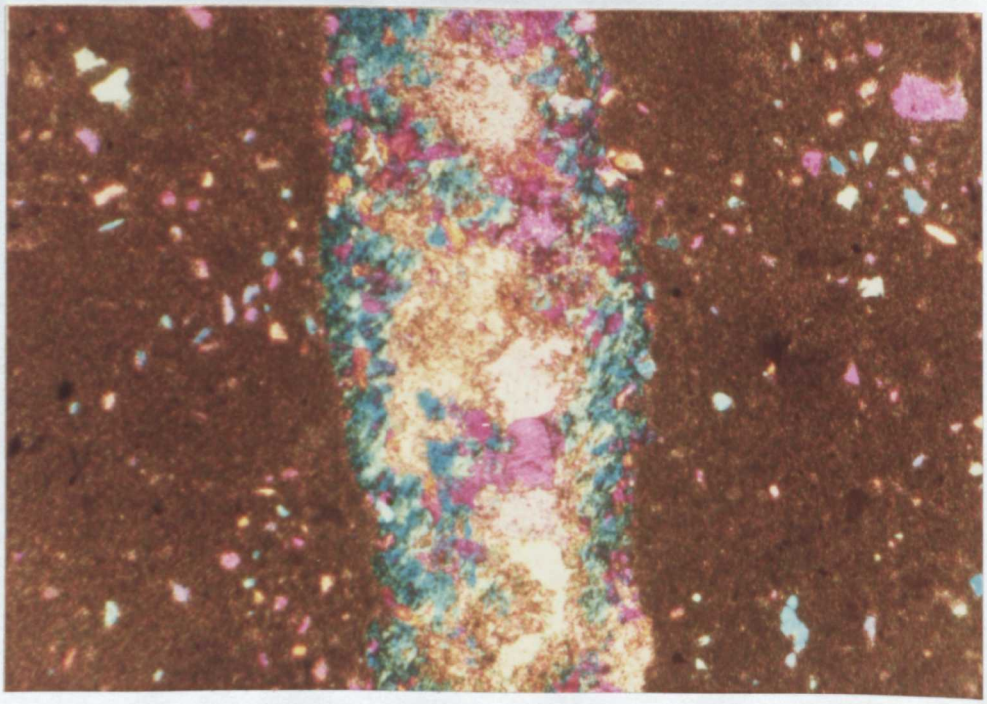
Veinlets of this type appear to be of multi-stage origin as indicated by cross-cutting of each other. Dolomite veinlets, however, have evidently formed in the earliest stage, at least in part, as evidenced by it being cut by a calcite veinlet (Plate 4.5).

Electron microprobe analysis has shown that some of the dolomite veinlets are composed of ferroan-dolomite, between C 2.4 and 3.2 percent of FeO are contained (Table 6.26).

4.7 Double- Mineral Veinlet

Cases where veinlets are filled with two different minerals are found of common occurrence. In this type, generally calcite appears to be the prevailing mineral, gypsum comes second in importance; whereas dolomite occurrences are relatively minor (Plate 4.4). However, either of these minerals can be the dominant in a given veinlet.

As/



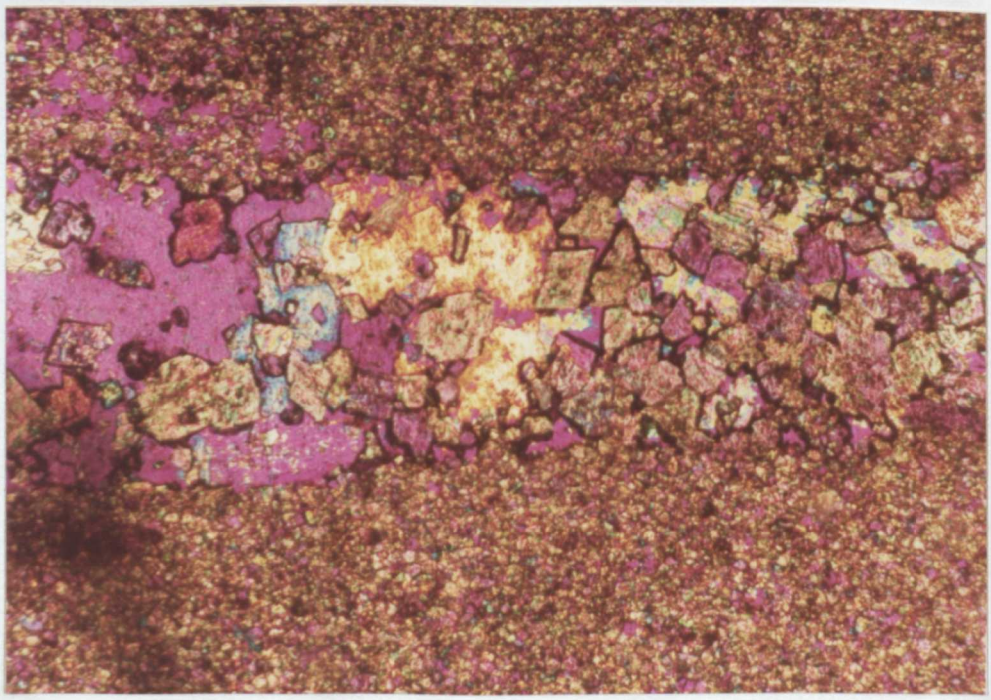


Plate 4.4

Upper: Microphotograph showing the occurrence of calcite and gypsum in the same veinlet. Calcite purple-pink. Under crossed nicols. Mag. 10X.
Loch Thom.

Lower: Microphotograph showing the occurrence of dolomite and gypsum in the same veinlet. Gypsum is yellowish. Under crossed nicols. Mag. 25X.
Overtoun Burn, near Dumbarton.

As its name signifies, this type is found composed of a combination of two different minerals. Their proportions are considerably variable in almost every case. When dolomite is involved, it usually occurs near the walls, however, scattered crystals do occasionally occur within the framework of its associate.

Generally the dominant mineral is most likely to be a chemical precipitate in origin. This, as explained in the case of the monomineralic veinlets is assumed on the grounds of the mode of growth of the crystals. They are always normal to the walls and increase in size towards the centres. The minor mineral may have formed also as a primary chemical precipitate, especially when it occurs near the walls or at the centre of the veinlet. The possibility of this minor mineral being of secondary origin, replacing its companion, particularly in the cases of its occurence in a scattered fashion, is possibly equally valid.

In case both minerals are primary in origin, it can be assumed that they have formed one after the other. The first stage of crystallization yielded the mineral near the walls. The following stage is believed to have begun as the precipitating solution had become depleted in the elements essential for the formation of the first mineral. This change in the chemistry of the groundwater may indicate an open system with new solutions bringing in fluids which precipitated the second mineral presently occupying the inner part of the veinlet.

4.7/

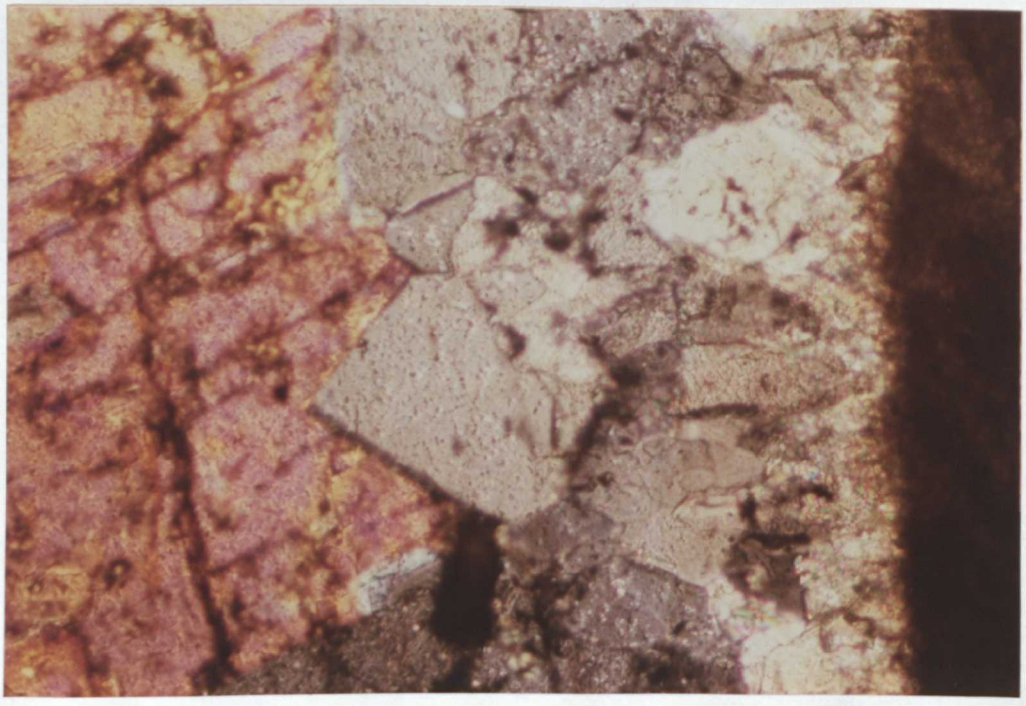
4.8 Treble-Mineral Veinlets

This type is found to be of a minor occurence compared with the other types. Its composition is evidently more complex than the others as demonstrated by the presence of three different minerals in the same veinlet - these are : dolomite; calcite; and celestine which occur in this order from the walls towards the centre (Plate 4.5, Table 6.28).

Both Schmidt (1965) and West et al (1968) and many others reported the occurrence of diagenetic celestine in veinlets. They believe when it is formed through replacement, the replaced mineral is usually calcite.

These minerals are likely to be all of primary origin through chemical precipitation. Both the dolomite and the calcite crystals show the same orientation, with respect to the walls, as that described for the other types. Furthermore, the calcite crystals even those of its first stage, are generally slightly coarser than those of the dolomite, on which they grow. These minerals may have formed in a similar manner as that proposed for the double-mineral type. Dolomite was the outcome of the first stage of crystallization, in which most, if not all, of the magnesium ions were used up. It was followed by calcite.Celestine may represent the final stage of the mineral crystallization in this veinlet. Replacement of either mineral, however is not clear, but it cannot be ruled out.

The/



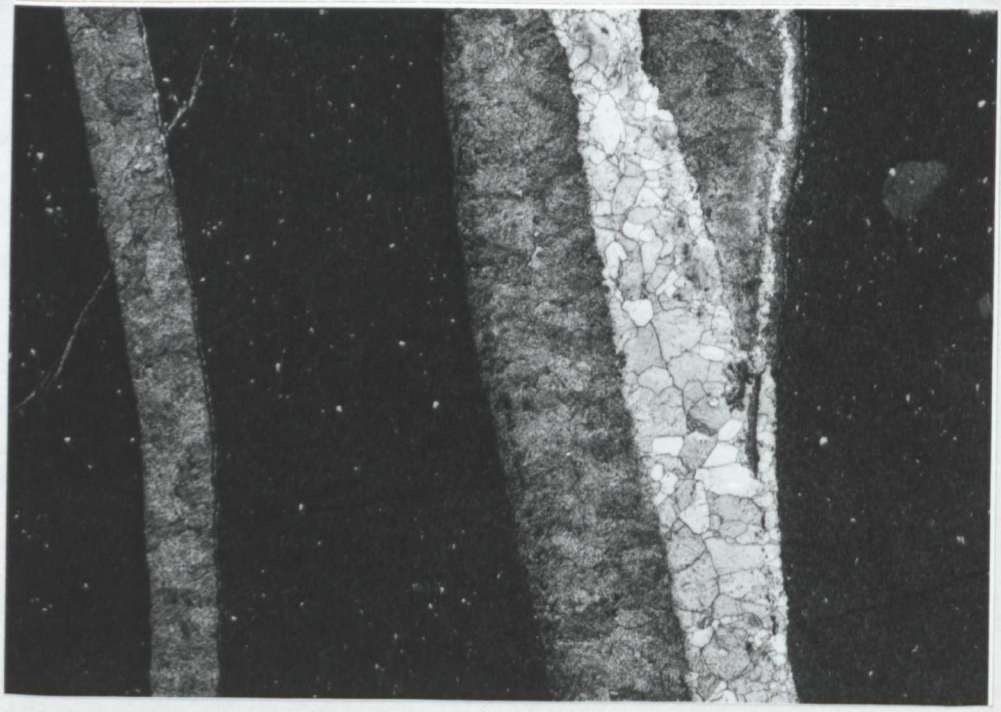


Plate 4.5

Upper: Microphotograph showing one side of a composite veinlet. Dolomite near the wall, followed by calcite, and celestine on the left. Under crossed nicols. Mag. 25X.

Overtoun Burn, near Dumbarton.

Lower: Photograph of a thin section showing a calcite veinlet cutting a dolomite veinlet. Mag. 10X.

Overtoun Burn, near Dumbarton.

The adhesion of dolomite, wherever present, to the walls of the veinlets, in almost every case, may hint at its primary precipitation. Since the parent rock (substrate) is dolomitic, it may have determined the first precipitative phase. Lindholm (1974) drew a similar conclusion.

CHAPTER FIVE

CARBONATE NODULES IN THE BALLAGAN FORMATION

5.1 Definition and Origin of Nodules

Occurrences of irregular carbonate bodies generally referred to as nodules, have been recorded from a wide range of formations from many parts over the world, at several different stratigraphical levels. Critical investigations of these peculiar bodies, however, are sporadic, although, they have been recognized as early as 1835, by Sedgwick (1835, in Garwood, 1891). These carbonate bodies are generally termed concretionary and nodular. Such terms were obviously used by investigators without any precise meaning, until Pettijohn (1957) defined true concretions as : - normally spherical, though, commonly very oblate, to irregular bodies formed generally by orderly precipitation of mineral matter in the pores of a sediment adjacent to a nucleus.

Septarian nodules are those nodules characterized by a series of radiating cracks that widen toward the centre, the cracks are almost invariably filled with a crystalline deposit, most commonly calcite.

In this study, the use of the term nodule will still be generally applied and those nodules with septarian structure will be simply referred to as nodules with septarian structure.

No/

No attempt at reviewing the literature on the subject is undertaken and reference should be made in this respect to Raiswell (1971). However, some of the widely accepted views are summarized and/or referred to wherever felt necessary.

Generally, the workers in this field had concentrated their investigations, partly or wholly, on the mode of formation and composition of the different types of these carbonate bodies, and their age with respect to the enclosing sediments.

Garwood (1891) proposed two possibilities as to the proximate source of the constituting carbonate material, one is that it was introduced into the concretionary bed subsequent to its formation in solution from outside, and the other was that it was deposited contemporaneously and subsequently segregated in situ, however, he favours the second.

Deegan (1971) believed that the possible mode of nodule formation involves fluctuation of pH around the threshold value necessary for carbonate crystallization. Pantin (1958) assumed that the carbonate material forming the diagenetic nodules was from organic or detrital carbonates distributed through the enclosing sediments.

Dickson and Barber (1976) found that nodules formed in four stages represented by two carbonate zones one chalcedony zone and one carbonate zone respectively.

Barber (1968) proposed two models for the formation of nodules. The first is the growth of a spherical nodule by ionic diffusion and precipitation from stagnant ground-water. Stagnant ground-water is/

is thought to be a necessary condition as may occur in impervious muds and shales. The second model involves slow ground-water flow along with diffusion of precipitating matter onto the spherical nodule surface. This case, he thought, is probably better suited to porous sands and sandstones.

Raiswell (1976) attributed the formation of nodules to the existence of an active accumulation of micro-organisms, i.e. the kinetics of microbiological processes are the critical factor in determining whether nodular growth occurs.

Lipmann (1955, in Raiswell, 1971); Seibold (1962, in Raiswell, 1971); and Raiswell (1971) were able to determine the approximate porosity of the enclosing sediments at the time of nodular growth, they all found that the growth can take place in sediments with porosity ranging from 70 to 75% while the latter had also found that it may occur in sediments with 40% porosity.

Nichols (1966) reported some nodules containing small bioclasts where others passed into and lie on top of colonies of corals. The laminae of the surrounding material is mainly bioclastic calcarenites with a matrix of cryptocrystalline calcite, carbonaceous material and some calcite silt. The laminae usually conform to the shape of the nodule. He recorded that peripheral cracks contain some of the surrounding calcarenite. With respect to the laminations within some nodules, he observed that they are not continuous with the laminae around them.

Noble/

Noble and Howells (1974) believed that nodules form in an early diagenetic environment soon after deposition. They believe the process to occur near the sediment-water interface with a rate of sedimentation not high enough to separate the zone of cementation from the overlying seawater before the nodules have been formed. Wanless (1979) proposed that nodular limestones are products of pressure solution. Fuzesy (1980) interpreted nodular limestone as early eogenetic in origin similar to inferred origin by Noble and Howells (1974). He believes that nodular formation took place soon after deposition of the sediments, by mineral segregation within lime-rich layers. He also reported that the flatness of some nodules and their compaction was caused by the weight of the overlying sediments.

Kaldi (1980) identified two types of nodules. One type he believes is analogous to present day nodules described from the Mediterranean (Muller & Fabricius, 1974). These nodules were reported to form as early cemented structures about 0.05 to 0.50 metre below the sediment water interface. One of the controls over nodule formation was believed to be the rate of sedimentation (see also Noble and Howells, 1974). While the other nodule type, because of lack of bedding and its chaotic orientation, it is believed was formed when the first type nodules were disturbed and redeposited as clasts in various stages of lithification.

Several classification schemes dealing with the origin of carbonate nodules were proposed by different writers, these range from/

from primary (contemporaneous) to secondary (late diagenetic). Pantin (1958) divided nodules into three types :-

a. Syngenetic :- Formed on the sea-bed at the time of deposition of the enclosing sediment.

b. Diagenetic:- Formed (probably within a few thousand years) after the deposition of the enclosing sediment, but before the various processes of compaction and consolidation were complete.

c. Epigenetic:- Formed after the compaction and consolidation of the enclosing sediment.

Similar schemes were proposed by Tarr (1921); Richardson (1921); and Weeks (1957). Tarr (1921), however, favoured the syngenetic origin for nodules he investigated and listed nine criteria as an evidence for such origin. Weeks (1957) included the diagenetic division into that of the syngenetic and attributed the alignment of nodules along a plane to a diastem or a brief period of non-deposition, while Tarr (1921) seem to have included this stage in that of the epigenetic.

Crimes (1966) added an additional three possible origins of nodules, these are :-

1. Allogenetic:- Derived from early formed sediments and deposited contemporaneously with the enclosing sediments.

2. Perigenetic:- Formed at one point, transported and then enclosed within sediment of virtually the same age.

3./

3. Metamorphic:- Formed as a result of metamorphism.

5.2 Nodules in the Ballagan Formation and their Origin

Nodular layers constitute a considerable proportion of the carbonates of the Ballagan Formation. They are found aligned parallel to the bedding. They are widely to closely spaced and in some instances coalesce to the point of forming a bed which may easily be mistaken for a layered carbonate unit. In some other cases, they are widely spaced resulting in the presence of only a few over tens of metres distance.

Although, the nodules are usually embedded in lutites, an exceptional case occurs in the section of Loch Thom, where they are found lying in a less pure carbonate layer which peels off easily leaving the nodules with a relatively smooth surface (Plate 5.1).

Nodules are random in their occurrence. They are found in association with sandstone; stratified carbonates (Figs. 5.2-4) and evidently mainly with lutites, which embedded also the nodules in the first two situations. They are also found laterally replaced by stratified carbonates (Plate 2.1, Fig. 5.7) and sandstone (Fig. 5.6). Several superimposed nodular layers occur enclosed in stratified carbonates (Fig. 5.5).

The nodules assume several different shapes: semi-spherical; oval; bulbous; flat; and most common of all, bodies with uneven surface. The bases are generally slightly flatter than the tops. Their boundary with the enclosing lutites is usually sharp. The horizontal/

Plate 5.1

Upper: Photograph showing nodules embedded into a more argillaceous carbonate layer.

Loch Thom.

Lower: Photograph showing development of secondary, coarsely crystalline minerals (septarian structure?), in a carbonate nodule.

Loch Thom.

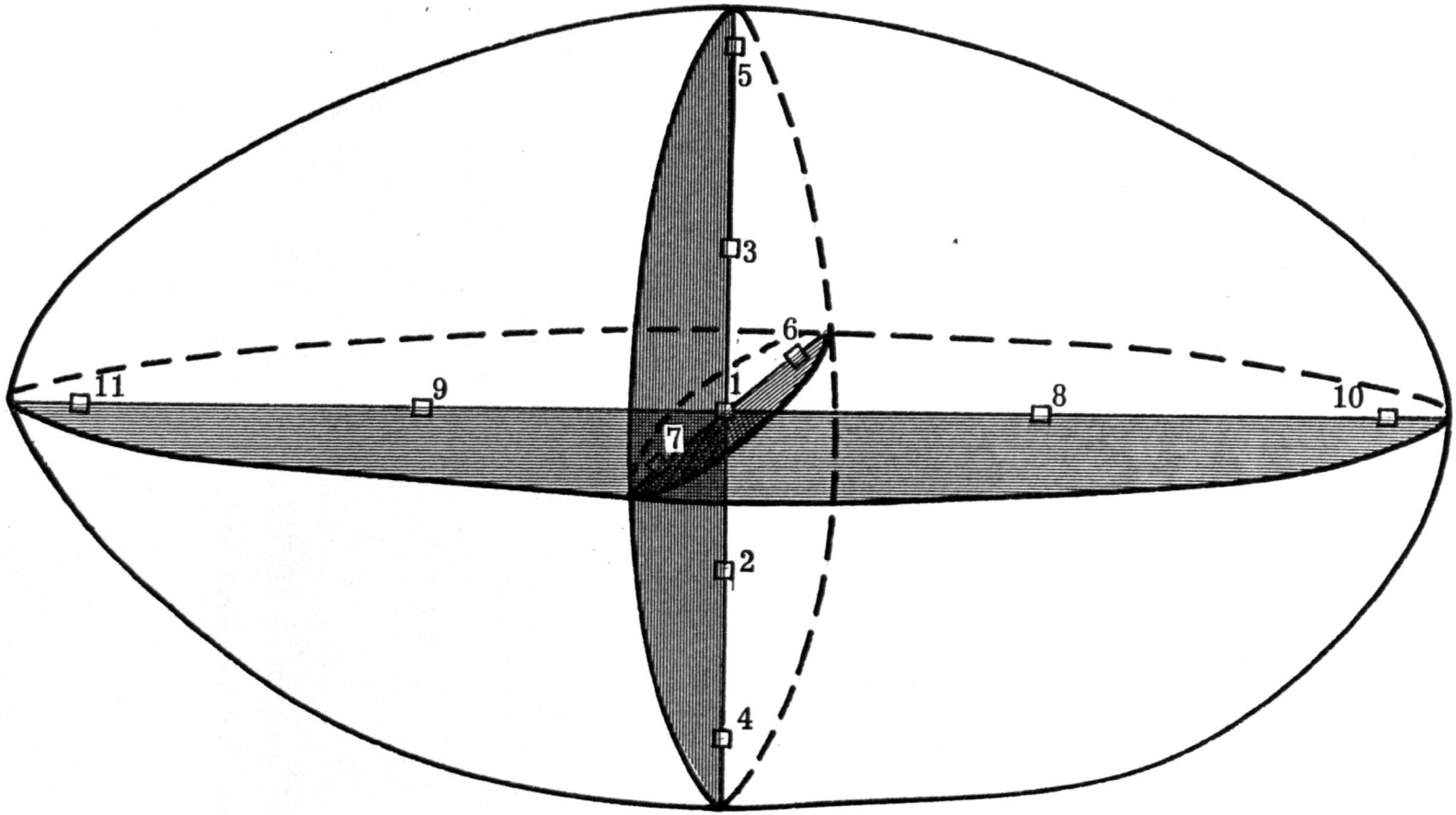


Fig. 5.1 : A carbonate nodule showing the positions of thin sections and chemical analyses. (For analyses see Tables 6.8A and 6.8B). Scale 1:10

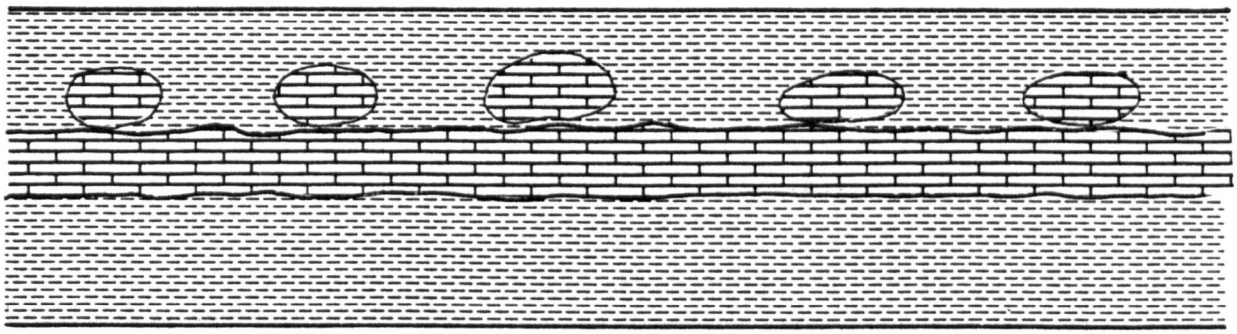


Fig. 5.2 : Sketch showing a nodular carbonate bed underlain by another stratified bed. Not to scale.

Carbonate Nodule
Stratified Carbonate
Lutites

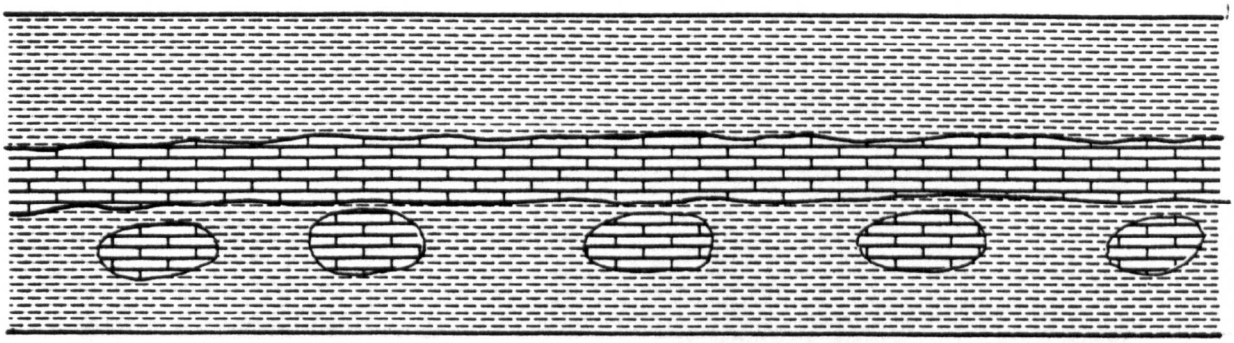


Fig. 5.3 : Sketch showing a nodular carbonate bed overlain by another stratified bed. Not to scale.

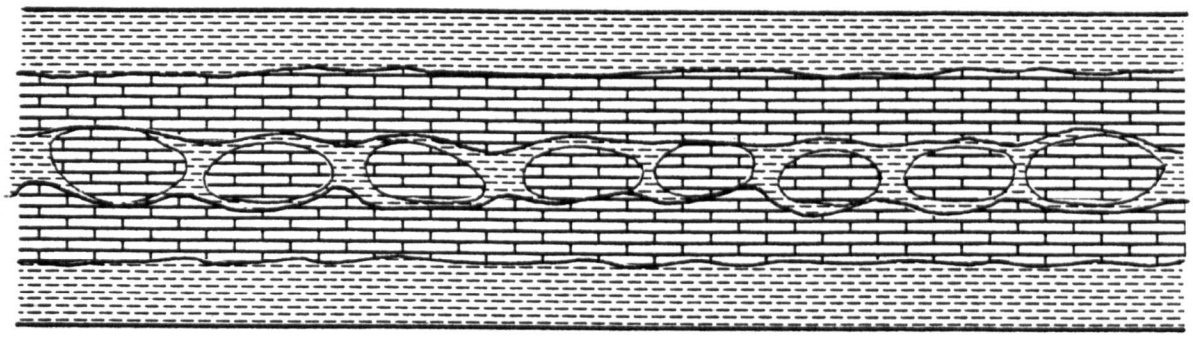


Fig. 5.4 : Sketch showing a nodular carbonate bed bordered by another two stratified beds. Not to scale.

Carbonate Nodule
Stratified Carbonate
Lutites

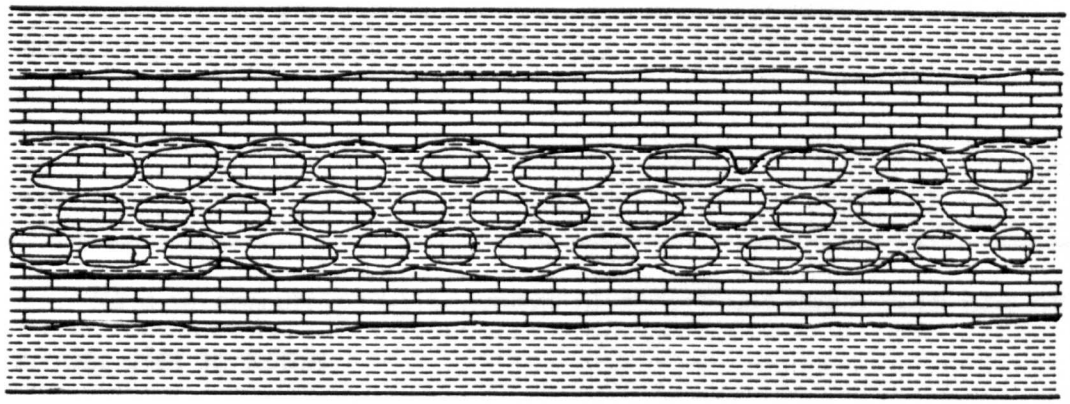


Fig. 5.5 : Sketch showing occurence of more than one nodular carbonate bed between another two stratified beds. Not to scale

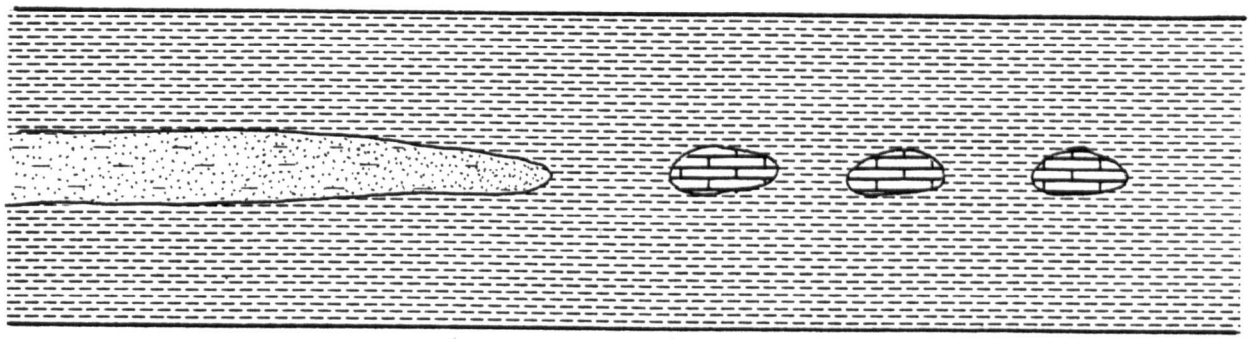


Fig. 5.6 : Sketch showing lateral replacement of a very sandy bed by a nodular carbonate bed. Not to scale.

Carbonate Nodule
Stratified Carbonate
Lutites
Sandstone

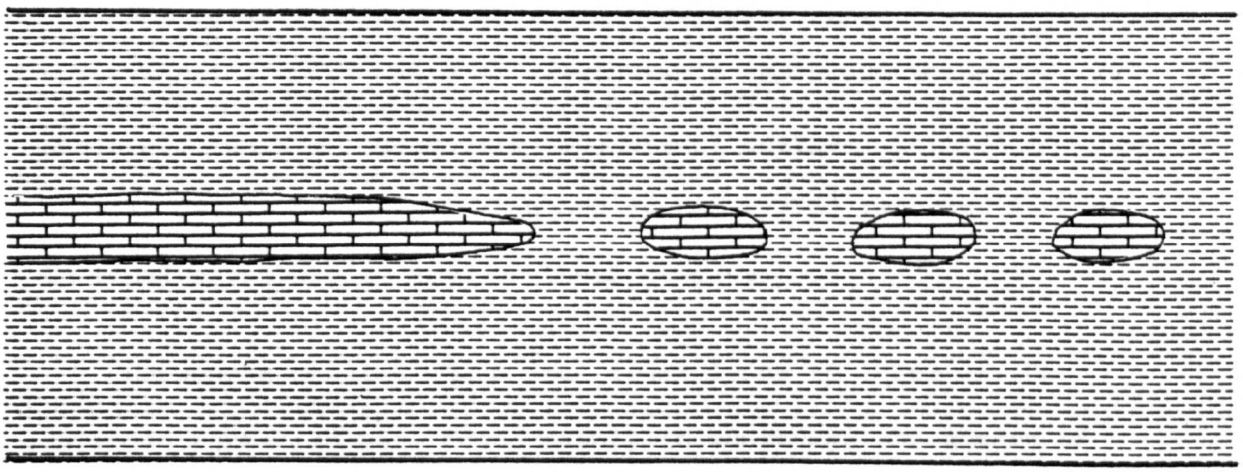


Fig. 5.7. : Sketch showing replacement of stratified carbonate bed by a nodular one. Not to scale.

horizontal dimensions of individual nodules are generally less than 0.25 metre, but reaches up to 0.50 metre. In vertical dimension (thickness) they range up to 0.35 metre (averaging c 0.15 metre).

The elongation of nodules along the bedding is attributed mainly to compaction, but preferential growth may have played a certain role in this elongation. H.C. Sorby (in Richardson, 1921) considered that the shape of nodules depended on that of their nuclei, this possibility is ruled out as the nodules under investigation contain no nuclei. However, Richardson (1921) ascribed the longer horizontal diameter to the same effect, compaction,while nodules are semi-consolidated.

The nodules lack any internal structure, apart from occasional occurrences of what could be considered a septarian structure, as the centre part of the nodule consists of coarsely crystalline mineral (Plate 5.1). Dickson and Barber (1976) reported lack of internal structure in some of their nodules.

Carbonate nodules which bear resemblance to those of the Ballagan Formation were found mainly in mudstones and shales of various ages (Richardson, 1921; Tarr, 1921; Weeks, 1953, 1957; Crimes 1966; Riaswell, 1971, Pantin, 1958; and Clifton, 1957, in Hayes 1964). Most of these workers favoured syngenetic and/or early diagenetic origin for concerned nodules. It can be deduced, therefore, that there is a general consensus amongst geologists as to the systems in which carbonate nodules grow: They believed them to be/

be both open and closed to the sea-water. For criteria used in identifying such systems, reference should be made to Raiswell (1971, pages 148-150).

Carbonate nodules of the Ballagan Formation are composed predominantly of nearly uniform carbonate grains with variable proportions of disseminated clay and sand particles similar to the majority of the variously investigated nodules recorded in the literature. They are devoid of any organic matter, Tarr (1921) however, reported that some nodules contain fossils in the outer parts or on the upper surface; Weeks (1957) found ammonites as their most common inclusions. Dickson and Barber (1976) observed randomly oriented skeletal debris as well as evidence for burrowing which was noticed by Hallam (1962). Hudson (1978) discovered that they contain uncrushed or only partly crushed fossils.

In addition to several individual thin-sections and chemical analyses, prepared from nodular carbonate beds in the Ballagan Formation, a nodule was cut into three perpendicular sections, one parallel to the bedding. The purpose was to examine whether it contains any internal structure. This nodule, however, proved to lack internal structure of any kind except a few small veinlets, it was found composed only of homogeneous carbonate crystals with randomly distributed sand grains. Also there is no evidence of any organic remains.

Along each of these surfaces thin-sections were prepared and chemical/

chemical analyses were carried out to determine the fabric and chemical composition of the constituting material (Fig. 5.1). The examination of these thin-sections shows that there is actually no textural difference throughout the said nodule. Also the results of the X-ray fluorescence analyses prove its similar composition throughout (Tables 8A and 8B).

The results of thin-sections examination and X-ray fluorescence analyses show that both nodular and layered carbonates of the Ballagan Formation in the area of study, are of similar texture and composition evidenced by the occurrence of the three microfacies in both of them indiscriminately. Furthermore, it has been found that almost all structures, such as veins, cavities, coarser mosaics, and shrinkage cracks, contained in the stratified carbonate layers are present, although some of them on a relatively smaller scale, in the nodular layers as well. Therefore, the diagenetic history of both the carbonates is thought to be similar. Microfacies A, present in the nodules, is thought to have been primary in the sense that it was precipitated and accumulated alongside lutite to form an initially carbonate-rich lutite. Conversion to a nodular form resulted when pore water migrated to the site of nodule formation, where, as a primary precipitate carbonate displaced lutite during nodule growth.

The author proposes a syngentic origin for the carbonate nodules of the Ballagan Formation on the basis of the following :

1. The microfacies present in the stratified beds are also present in the nodules (see Figs. 3.6-12).
2. There are no more quartz grains, clays, or any other terrigenous components in nodules than there are in the stratified beds.

3./

3. The overall chemical composition of the nodules resembles the composition of the stratified units.

4. No systematic changes in petrography or composition occur through the nodules.

5. Their enclosing beds are not permeable, and the nodules do not occur in permeable horizons. They are enclosed in impermeable shales and mudstones.

6. The external surfaces of the nodules (i.e. in some cases all around them) contain shrinkage cracks. As with the stratified beds, this implies a reduction in the volume of the original carbonate.

7. The association of nodules with stratified carbonate beds and sandstone.

8. The arrangement of nodules in planes parallel to the formation bedding.

9. The recurrence of nodular layers throughout the formation section.

10. The lateral replacement of nodules by stratified carbonates and sandstone.

11. The occurrence of superimposed nodular beds.

The/

The similarity in structure and composition between the laterally persistent and nodular carbonate beds in the Ballagan Formation implies a similar origin. This origin is unlikely to involve a great deal of fluid migration within the sediment, as these sediments are quite impermeable. However, nodules do commonly occur in shales before compaction. Due to the absence of laminations in the shale, the investigator has been deprived of an important tool used in the reconstruction of the nodule's history.

The carbonate nodules in the Ballagan Formation are believed likely to have formed by an accretionary process involving the constituent carbonate crystals subsequent to their deposition. Chemical precipitation of these particles most probably took place in or very close to the level where nodules are presently found.

The accretionary process, which may have occurred around a nucleus, presumably of similar origin, however, is suggested to have begun when the enclosing sediments were still unconsolidated, i.e. the nodules are of a syngenetic origin of Tarr (1921); Weeks (1957); and Crimes (1966).

CHAPTER SIX

GEOCHEMISTRY

As described in the preceding parts of this study, the rocks concerned are fine-grained, homogeneous and lack any fossils. Therefore, a geochemical study of these sedimentary rocks was undertaken to throw some light on the original sedimentary processes responsible for their formation and the diagenetic processes involved. Both X-ray fluorescence and electron microprobe were employed for this purpose, the first to determine the bulk composition of the rocks, and the latter to determine the mineral composition whenever possible.

6.1 X-Ray Fluorescence Analysis

Pressed pellets were prepared for analysis from selected samples of the carbonate layers in the Ballagan Formation. They were analysed for the oxides of ten major elements in addition to seventeen trace elements. The methods of Harvey et al (1973) were employed in the case of the major elements, and that of Leake et al (1969) for the trace elements.

Both Professor Leake and Dr. C. Farrow recommended the use of G. Tanner's samples the analyses of which were published in a paper by Leake et al (1975) as standards. Pressed pellets were prepared from these samples for the purpose of calibration.

The/

The use of these samples gave satisfactory results with the exception of SiO_2 which was found to give erroneous concentrations presumably due to the difference in the mineralogical mode of occurrence of Si in both rock types. In order to overcome this problem four samples representing a cross-section of the obtained SiO_2 content in the author's rocks were analysed for this oxide in the wet chemical laboratory and the SiO_2 content is corrected accordingly using the straight line equation.

$$Y = A_o + A_1X$$

The total iron is stated as Fe_2O_3. CO_2 and H_2O amounts were determined by wet chemical analysis. The CO_2 contents were satisfactory but those of H_2O were not reliable which has led to their computation on the basis of the computed mineral composition of the hydrous minerals, from the chemical analyses as will be described later in this section.

The analyses are tabulated for each section separately in Tables 1-7. Tables carrying the letter A contain the major oxides in addition to SO_3, SrO and BaO as calculated from the contents of S, Sr and Ba respectively, and the computed mineral proportions. Tables carrying the letter B contain the trace elements.

The /

The objectives of any geochemical analysis in addition to the determination of the compositional elements and their concentrations are obviously to establish any possible relationship between the analysed elements and to compute the mineralogical compositions of the rocks and from this information reconstruct the history of the studied rocks. Numerous plots have been made to establish correlations between elements.

The Al is considered to be almost exclusively in the clay minerals a view also followed by Weber (1964). Hence, Al_2O_3 is believed to be a valid indicator of the content of clay minerals in general and this obviously influenced the concentrations of several other elements which are also present in typical clay minerals such as K, Fe and Mg and many trace elements.

Plots involving Al_2O_3 fall into three different categories :

A. Plots which are showing a fair positive correlation with Al_2O_3 such as SiO_2, TiO_2, Fe_2O_3, K_2O, Cr, Ni, Rb, Ga, and Th (Figs. 6.1-9). The slight disturbance of such correlation in the case of SiO_2 is obviously caused by the presence of free SiO_2 in the form of detrital quartz and feldspar as shown by microscopic study. With K_2O and Fe_2O_3 plots, the positive correlation is disturbed by the samples from Little Corrie and Ballagan Glen Sections which are likely to contain either clay minerals with different compositions, namely, with more Fe_2O_3 and possibly less/

less K_2O, or by the actual presence of haematite which has been deduced from the rock composition. As it will be shown later K_2O - content has been successfully used to compute the content of illite.

B. Plots showing a poor positive correlation with Al_2O_3 include MgO, Co, Zn and Zr (Figs. 6.10-13). The reason for such poor correlation of these elements with the exception of Mg is not clear but variations in the source area where they are derived from may be the explanation. In the MgO plot, the positive correlation is good in low MgO values which may indicate that the source of this oxide in these samples was predominantly in the clay.

C. Plots showing no correlation with Al_2O_3 include Na_2O, P_2O_5, MnO, La, Cu, Y, Ba, Pb and Ce. Lack of correlation can be attributed to variation in composition of the parent rock. Furthermore, loss or gain of some elements may occur during transport as in the case of Cu and Pb. Shaw (1954) suggests they go into solution as soluble cations and become trapped in the clay sediments by sorption, this process will affect their contents and consequently causes disturbance of correlation. MnO is associated with carbonates whereas Ba with sulphates.

The/

The major minerals, dolomite and calcite, probably take only a very few elements such as Mn and Sr in solid solution in significant amounts. Graf (1962) and Weber (1964) have suggested that the trace elements in carbonate rocks mainly depend on the non-carbonate minerals, especially clay minerals, including detrital minerals, accessory authigenic precipitates, organic matter, phases formed during diagenesis and the elements absorbed upon all of these materials. The clay minerals probably supplied most of the trace elements as shown earlier.

S plotted against CaO does not reveal any significant correlation showing that the amount of CaO combined with S in gypsum is generally very low and most of the Ca is in carbonate.

Plots of S against Sr and Ba both separately and combined (Figs. 6.14-16) all show a moderate positive correlation when more than 1,000 ppm of each element is present indicating the presence of celestine and baryte.

Ba was observed by Friedman (1969) to be low in marine limestones (less than 60 ppm) and higher in freshwater limestones (more than 60 ppm). The present Ba - contents are rather high which might be due to the mixing of continental and marine brines and this would be consistent with a chemical precipitation origin for the present dolomites.

Chemical/

Chemical analyses across a carbonate nodule are shown in Tables 8A and 8B. These analyses are similar, and, therefore, indicate a homogeneous composition of the nodule. Furthermore, this composition is similar to those of many carbonate horizons, both nodular and stratified. Thus, it may indicate that the constituents were formed in the same manner as the rest of the carbonate horizons. The mode of formation of the nodules is discussed under a separate heading.

Table 6.1A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Loch Thom						
	MG 33	MG 34	MG 35	MG 36	MG 37	MG 38	MG 39
SiO_2	12.62	7.81	4.25	26.45	15.00	13.80	9.99
Al_2O_3	4.35	5.06	2.81	3.70	4.22	5.64	5.18
TiO_2	0.18	0.15	0.10	0.13	0.12	0.15	0.16
Fe_2O_3	1.57	2.56	1.18	1.62	1.63	1.72	1.82
MnO	0.23	0.20	0.22	0.18	0.11	0.09	0.19
MgO	12.86	13.91	16.23	7.04	3.11	2.38	9.44
CaO	28.52	28.95	31.53	28.35	39.27	39.58	33.87
Na_2O	0.27	0.22	0.23	0.23	0.19	0.19	0.20
K_2O	0.92	1.12	0.82	1.11	1.21	1.50	1.24
P_2O_5	0.12	0.14	0.14	0.63	0.17	0.22	0.11
H_2O	1.38	1.29	0.94	1.38	1.55	1.90	1.82
CO_2	35.43	37.95	41.95	28.93	33.22	32.68	35.16
SO_3	0.52	-	0.30	0.25	0.35	0.25	0.40
Sr O	0.11	-	-	-	-	-	0.25
BaO	0.48	-	-	-	-	-	-
Total A	99.56	99.36	100.70	100.00	100.15	100.10	99.83
Calcite	20.76	17.03	16.39	34.79	63.75	66.39	40.42
Dolomite	55.11	63.82	72.79	28.57	10.87	7.31	36.43
Total B	75.87	80.85	89.18	63.36	74.62	73.70	76.85
Gypsum	0.40	-	0.65	0.54	0.75	0.54	0.45
Celestine	0.19	-	-	-	-	-	0.44
Barytes	0.73	-	-	-	-	-	-
Illite	14.17	17.24	10.72	17.07	18.64	22.84	18.88
Chlorite	-	-	-	-	-	-	2.35
Montmor.	4.80	-	-	-	-	1.29	-
Total C	18.97	17.24	10.72	17.07	18.64	24.13	21.23
Quartz	2.37	-	-	17.96	5.05	1.47	-
Haematite	-	0.66	-	-	-	-	-
Total D	98.53	98.75	100.55	98.93	99.06	99.84	98.97

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.1A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Loch Thom		
	MG 40	MG 103	MG 104
SiO_2	4.02	3.61	1.86
Al_2O_3	2.76	1.91	0.62
TiO_2	0.10	0.04	0.05
Fe_2O_3	1.00	0.59	0.62
MnO	0.26	0.09	0.23
MgO	16.14	1.04	14.14
CaO	32.09	49.84	35.99
Na_2O	0.23	0.14	0.23
K_2O	0.70	0.52	0.34
P_2O_5	0.18	0.14	0.15
H_2O	0.99	0.76	0.55
CO_2	42.03	39.70	43.53
SO_3	0.42	0.35	0.55
Sr O	-	-	0.12
BaO	-	-	0.18
Total A	100.81	98.73	100.02
Calcite	17.91	86.93	28.55
Dolomite	71.56	2.93	64.90
Total B	89.47	89.86	93.45
Gypsum	0.90	0.75	0.79
Celestine	-	-	0.21
Barytes	-	-	0.27
Illite	9.07	7.92	5.24
Chlorite	-	-	-
Montmor.	-	-	-
Total C	9.07	7.92	5.24
Quartz	-	-	-
Haematite	-	-	-
Total D	99.44	98.53	99.96

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.18: Chemical analyses of carbonate beds in the Ballagan Formation.

	Loch Thom						
	MG 33	MG 34	MG 35	MG 36	MG 37	MG 38	MG 39
S	2118	889	1175	1030	1384	1042	1573
Cr	22	33	16	26	23	24	22
Co	5	15	10	7	8	5	ND
Ni	2	4	3	3	2	3	3
Cu	3	ND	7	26	ND	ND	ND
Zn	17	23	27	28	24	21	25
Ga	3	6	3	5	5	9	5
Rb	32	44	31	39	39	52	47
Sr	921	643	336	930	716	620	2093
Y	19	28	33	46	17	15	13
Zr	44	20	22	19	22	29	14
Nb	6	12	13	5	8	10	7
Ba	4323	818	97	225	64	59	756
La	48	36	47	59	20	23	23
Pb	ND	2	1	8	ND	4	1
Ce	119	119	144	166	127	116	93
Th	3	ND	2	5	7	3	6

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.1B: Chemical analyses of carbonate beds in the Ballagan Formation.

	Loch Thom		
	MG 40	MG 103	MG 104
S	1719	1430	2235
Cr	15	8	9
Co	6	9	5
Ni	ND	ND	ND
Cu	ND	ND	ND
Zn	24	3	22
Ga	5	1	2
Rb	27	16	14
Sr	560	411	988
Y	29	5	10
Zr	14	22	3
Nb	9	4	7
Ba	169	1	1591
La	44	7	12
Pb	7	2	7
Ce	155	127	109
Th	6	2	4

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.2A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Ben Bowie, Helensburgh						
	MG 41	MG 43	MG 42	MG 44	MG 45	MG 46	MG 47
SiO_2	13.63	2.16	3.64	3.49	41.08	15.14	7.57
Al_2O_3	5.26	0.73	2.40	2.07	4.37	6.91	3.54
TiO_2	0.19	0.01	0.08	0.08	0.16	0.20	0.11
Fe_2O_3	1.57	0.27	0.84	0.74	0.65	2.00	1.11
MnO	0.27	0.15	0.44	0.31	0.10	0.13	0.35
MgO	13.26	2.26	15.45	16.25	1.36	2.36	15.67
CaO	28.11	45.76	32.80	32.71	24.96	38.46	31.50
Na_2O	0.25	0.15	0.22	0.24	0.38	0.22	0.21
K_2O	1.06	0.05	0.56	0.59	1.42	1.79	0.68
P_2O_5	0.14	0.05	0.17	0.13	0.07	0.24	0.15
H_2O	1.74	1.52	0.83	0.84	1.90	2.28	0.96
CO_2	35.14	36.70	42.45	42.82	20.13	30.92	40.35
SO_3	0.35	5.84	0.42	0.35	1.45	0.27	-
Sr O	-	3.56	-	-	0.50	-	-
BaO	-	0.25	-	-	0.88	-	-
Total A	100.97	99.46	100.20	100.62	99.41	100.92	101.25
Calcite	19.55	72.47	19.49	18.50	41.80	64.29	20.67
Dolomite	55.62	10.13	70.99	72.67	3.67	5.56	65.49
Total B	75.17	82.60	90.48	91.17	45.47	69.85	86.16
Gypsum	0.75	6.37	0.90	0.75	1.30	0.58	-
Celestine	-	6.31	-	-	0.88	-	-
Barytes	-	0.37	-	-	1.34	-	-
Illite	16.15	0.78	8.61	8.98	21.20	27.26	10.46
Chlorite	1.45	-	-	-	-	-	-
Montmor.	3.53	2.76	-	-	-	2.17	3.55
Total C	21.13	3.54	8.61	8.98	21.20	29.43	14.01
Quartz	2.85	-	-	-	30.21	-	-
Haematite	-	-	-	-	-	-	-
Total D	99.90	99.19	99.99	100.90	100.40	99.86	100.17

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.2A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Ben Bowie, Helensburgh			
	MG 48	MG 49	MG 51	MG 52
SiO_2	7.45	13.20	7.30	45.16
Al_2O_3	3.16	6.79	3.10	13.10
TiO_2	0.10	0.20	0.09	0.58
Fe_2O_3	1.22	2.42	1.15	4.49
MnO	0.35	0.15	0.36	0.06
MgO	14.61	2.80	13.13	4.96
CaO	31.17	37.44	33.19	14.51
Na_2O	0.21	0.21	0.19	0.27
K_2O	0.64	1.50	0.63	1.63
P_2O_5	0.14	0.11	0.15	0.12
H_2O	1.05	2.01	1.02	4.14
CO_2	39.64	31.25	40.22	11.39
SO_3	0.27	0.60	0.25	-
Sr O	-	0.48	-	-
BaO	-	-	-	-
Total A	100.01	99.16	100.78	100.56
Calcite	18.43	62.01	26.38	25.90
Dolomite	66.07	8.35	59.97	-
Total B	84.50	70.36	86.35	25.90
Gypsum	0.58	0.48	0.54	-
Celestine	-	0.86	-	-
Barytes	-	-	-	-
Illite	9.85	23.07	9.71	25.07
Chlorite	-	-	-	13.53
Montmor.	4.45	3.84	3.71	14.00
Total C	14.30	26.91	13.42	52.60
Quartz	-	-	-	20.80
Haematite	-	-	-	-
Total D	99.38	98.61	100.31	99.30

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.28: Chemical analyses of carbonate beds in the Ballagan Formation.

	Ben Bowie, Helensburgh						
	MG 41	MG 43	MG 42	MG 44	MG 45	MG 46	MG 47
S	1391	23356	1696	1351	5774	1129	981
Cr	29	ND	16	ND	ND	ND	ND
Co	5	4	5	2	ND	10	ND
Ni	4	ND	ND	ND	ND	ND	ND
Cu	269	15	86	1	34	15	ND
Zn	20	71	22	17	11	21	16
Ga	6	32	3	2	6	5	2
Rb	40	9	20	18	35	59	27
Sr	226	30097	241	210	4247	367	147
Y	31	ND	19	22	3	19	13
Zr	71	ND	19	34	7	42	28
Nb	12	10	ND	12	ND	14	13
Ba	203	2177	52	50	7894	113	66
La	51	ND	26	29	ND	36	16
Pb	7	ND	18	10	ND	14	6
Ce	130	100	124	108	51	139	89
Th	8	ND	5	2	4	5	5

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.2B: Chemical analyses of carbonate beds in the Ballagan Formation.

	Ben Bowie, Helensburgh			
	MG 48	MG 49	MG 51	MG 52
S	1124	2438	1042	562
Cr	ND	25	14	25
Co	1	6	2	3
Ni	ND	5	ND	4
Cu	ND	76	15	7
Zn	22	30	15	41
Ga	2	9	2	12
Rb	26	53	23	103
Sr	187	4104	177	212
Y	14	5	17	21
Zr	25	ND	22	218
Nb	11	2	12	14
Ba	51	376	41	274
La	20	9	18	18
Pb	6	6	13	2
Ce	101	109	107	60
Th	3	8	7	7

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.3A: Chemical analyses of carbonate beds in the Ballagan Formation

	Auchenreoch Glen						
	MG 24	MG 12	MG 13	MG 14	MG 15	MG 16	MG 17
SiO_2	3.80	6.30	16.58	10.02	4.19	17.04	9.52
Al_2O_3	2.16	3.32	7.31	2.57	2.47	8.00	4.91
TiO_2	0.08	0.11	0.22	0.09	0.09	0.24	0.17
Fe_2O_3	0.84	1.40	2.55	0.96	1.20	2.47	2.08
MnO	0.43	0.40	0.12	0.29	0.30	0.12	0.26
MgO	15.54	14.89	3.73	14.28	15.93	3.49	14.97
CaO	33.36	32.14	35.73	30.37	31.78	34.95	28.68
Na_2O	0.24	0.31	0.22	0.26	0.25	0.21	0.25
K_2O	0.58	0.82	1.72	0.74	0.70	1.87	1.21
P_2O_5	0.17	0.22	0.15	0.15	0.21	0.22	0.18
H_2O	0.87	1.15	2.78	1.01	0.94	2.81	1.53
CO_2	42.49	40.07	29.13	38.70	41.66	28.50	37.97
SO_3	0.45	0.47	0.35	0.35	0.32	0.35	0.30
Sr O	-	-	-	-	-	-	-
BaO	-	-	-	-	-	-	-
Total A	101.01	101.60	100.59	99.79	100.04	100.27	102.03
Calcite	21.32	22.42	60.42	19.52	17.89	59.07	15.27
Dolomite	69.38	63.30	5.37	63.10	70.80	5.30	65.49
Total B	90.70	85.72	65.79	82.62	88.69	64.37	80.76
Gypsum	0.97	1.01	0.75	0.75	0.69	0.75	0.65
Celestine	-	-	-	-	-	-	-
Barytes	-	-	-	-	-	-	-
Illite	8.84	12.61	26.46	11.28	10.78	28.49	18.64
Chlorite	-	-	5.02	-	-	3.91	-
Montmor.	-	-	-	-	-	-	0.37
Total C	8.84	12.61	31.48	11.28	10.78	32.40	19.01
Quartz	-	-	2.34	4.35	-	1.88	-
Haematite	-	-	-	-	-	-	-
Total D	100.51	99.34	100.36	99.00	100.16	99.40	100.42

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.3A: Chemical analyses of carbonate beds in the Ballagen Formation

	Auchenreoch Glen						
	MG 18	MG 19	MG 20	MG 21	MG 22	MG 25	MG 26
SiO_2	8.71	7.99	5.74	16.57	2.43	12.05	12.38
Al_2O_3	3.30	3.98	2.43	3.05	1.49	4.29	3.67
TiO_2	0.15	0.15	0.09	0.09	0.04	0.18	0.13
Fe_2O_3	1.80	2.00	1.20	0.91	0.62	1.42	1.43
MnO	0.36	0.22	0.21	0.26	0.27	0.19	0.27
MgO	14.08	15.17	15.29	14.29	10.88	14.44	13.92
CaO	31.04	28.83	31.65	26.53	40.00	28.06	28.72
Na_2O	0.26	0.21	0.22	0.24	0.18	0.21	0.22
K_2O	0.89	1.17	0.75	0.78	0.38	1.25	0.97
P_2O_5	0.21	0.06	0.10	0.15	0.15	0.04	0.10
H_2O	1.30	1.34	0.97	1.07	0.67	1.44	1.33
CO_2	38.88	38.36	40.87	35.46	42.72	36.63	36.93
SO_3	0.40	-	0.25	0.27	0.65	-	-
Sr O	-	-	-	-	0.19	-	-
BaO	-	-	-	-	-	-	-
Total A	101.38	99.48	99.77	99.67	100.67	100.20	100.34
Calcite	21.38	15.67	19.40	13.38	44.37	15.59	17.86
Dolomite	61.77	65.94	67.76	61.97	48.63	62.39	60.93
Total B	83.15	81.61	87.16	75.35	93.00	77.98	78.79
Gypsum	0.86	-	0.54	0.58	1.08	-	0.58
Celestine	-	-	-	-	0.34	-	-
Barytes	-	-	-	-	-	-	-
Illite	13.71	18.00	11.53	11.88	5.85	19.05	14.93
Chlorite	-	-	-	-	-	-	-
Montmor.	1.99	-	-	1.08	-	-	1.84
Total C	15.70	18.00	11.53	12.96	5.85	19.05	16.77
Quartz	0.61	-	-	9.88	-	2.48	3.73
Haematite	-	-	-	-	-	-	-
Total D	100.32	99.61	99.23	98.77	100.27	99.51	99.87

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.3A: Chemical analyses of carbonate beds in the Ballagan Formation

	Auchenreoch Glen						
	MG 27	MG 28	MG 5	MG 4	MG 3	MG 29	MG 31
SiO_2	17.58	6.84	4.46	3.32	22.15	10.71	16.87
Al_2O_3	5.72	2.92	2.22	1.90	9.49	4.10	5.38
TiO_2	0.21	0.09	0.09	0.07	0.31	0.14	0.16
Fe_2O_3	1.70	1.10	1.04	0.76	3.26	1.45	1.62
MnO	0.23	0.27	0.37	0.41	0.12	0.45	0.11
MgO	12.78	14.25	14.43	15.95	4.76	14.30	2.44
CaO	25.06	28.90	32.62	33.01	28.93	28.68	37.83
Na_2O	0.28	0.23	0.24	0.23	0.22	0.27	0.19
K_2O	1.40	0.58	0.49	0.46	1.79	0.91	1.42
P_2O_5	0.14	0.15	0.20	0.15	0.20	0.19	0.15
H_2O	1.89	0.90	0.94	0.74	3.26	1.39	2.19
CO_2	32.63	37.77	40.63	42.74	24.35	37.31	30.51
SO_3	0.30	2.15	1.60	1.10	0.32	0.52	1.15
Sr O	-	2.45	1.08	0.82	0.11	0.27	0.08
BaO	-	0.28	0.15	-	-	-	-
Total A	99.92	98.88	100.56	101.56	99.27	100.69	100.10
Calcite	14.49	16.99	22.32	19.46	47.30	16.75	63.30
Dolomite	55.01	63.49	64.57	71.62	7.44	62.75	5.61
Total B	69.50	80.48	86.89	91.08	54.74	79.50	68.91
Gypsum	0.65	0.24	1.48	1.00	0.51	0.67	2.02
Celestine	-	4.34	1.91	1.45	0.19	0.48	0.14
Barytes	-	0.43	0.23	-	-	-	-
Illite	21.32	8.93	7.54	7.07	27.53	14.00	21.63
Chlorite	-	-	-	-	6.86	-	1.05
Montmor.	2.81	3.66	1.41	-	4.14	4.05	-
Total C	24.13	12.59	8.95	7.07	38.53	18.05	22.68
Quartz	5.00	-	-	-	4.22	1.05	5.78
Haematite	-	-	-	-	-	-	-
Total D	99.28	98.08	99.46	100.60	98.19	99.75	99.53

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.3A: Chemical analyses of carbonate beds in the Ballagan Formation

	Auchenreoch Glen				
	MG 30	MG 32	MG 2	MG 1	MG 105
SiO_2	6.89	4.60	8.47	5.83	12.31
Al_2O_3	3.21	2.32	3.41	3.23	5.61
TiO_2	0.12	0.08	0.14	0.10	0.19
Fe_2O_3	1.08	0.80	1.78	1.49	1.86
MnO	0.31	0.30	0.35	0.22	0.14
MgO	15.46	15.13	14.41	15.00	5.50
CaO	30.99	32.82	29.81	31.58	37.01
Na_2O	0.23	0.23	0.25	0.21	0.22
K_2O	0.90	0.60	0.88	0.79	1.43
P_2O_5	0.17	0.21	0.20	0.21	0.29
H_2O	1.03	0.86	1.43	1.01	1.91
CO_2	40.57	41.65	38.03	40.50	33.84
SO_3	-	0.37	0.65	0.37	0.37
Sr O	-	-	-	0.20	-
BaO	-	-	-	-	-
Total A	100.96	99.97	99.81	100.74	100.68
Calcite	18.35	21.51	18.29	20.08	54.22
Dolomite	68.10	67.45	62.83	66.36	20.95
Total B	86.45	88.96	81.12	86.44	75.17
Gypsum	-	0.79	1.40	0.46	0.80
Celestine	-	-	-	0.35	-
Barytes	-	-	-	-	-
Illite	13.72	9.15	13.53	12.17	21.78
Chlorite	-	-	-	-	-
Montmor.	-	-	2.71	-	2.05
Total C	13.72	9.15	16.24	12.17	23.83
Quartz	-	-	-	-	-
Haematite	-	-	-	-	-
Total D	100.17	98.90	98.76	99.42	99.80

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.3B: Chemical analyses of carbonate beds in the Ballagan Formation.

	Auchenreoch Glen						
	MG 24	MG 12	MG 13	MG 14	MG 15	MG 16	MG 17
S	1760	1855	1443	1438	1305	1384	1207
Cr	13	19	29	14	16	30	25
Co	4	2	15	3	3	12	9
Ni	ND	1	6	ND	ND	8	3
Cu	ND	ND	ND	ND	ND	ND	ND
Zn	124	147	168	160	128	158	127
Ga	7	8	10	6	6	9	7
Rb	19	29	60	24	26	68	45
Sr	385	355	450	236	194	356	213
Y	14	16	14	19	9	18	31
Zr	14	25	55	43	19	40	27
Nb	6	6	8	7	6	7	ND
Ba	248	113	105	163	146	791	121
La	14	17	41	28	12	25	38
Pb	4	4	3	7	64	24	5
Ce	97	98	142	104	95	62	134
Th	2	2	7	6	5	6	10

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.38: Chemical analyses of carbonate beds in the Ballagan Formation.

	Auchenreoch Glen						
	MG 18	MG 19	MG 20	MG 21	MG 22	MG 25	MG 26
S	1618	631	1013	1138	2634	559	1081
Cr	22	22	12	17	9	22	18
Co	9	6	5	3	2	ND	7
Ni	3	4	ND	ND	ND	1	1
Cu	4	ND	ND	ND	5	ND	ND
Zn	107	123	121	87	56	160	155
Ga	7	7	6	6	6	7	7
Rb	30	40	23	27	9	38	32
Sr	311	249	242	201	1571	272	428
Y	30	42	25	15	42	23	22
Zr	38	32	22	27	ND	58	70
Nb	11	7	10	7	4	6	12
Ba	229	60	236	91	134	174	146
La	33	52	50	24	45	19	30
Pb	14	8	8	ND	ND	1	7
Ce	131	174	142	85	179	84	111
Th	3	7	6	3	4	4	2

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.38: Chemical analyses of carbonate beds in the Ballagan Formation.

	Auchenreoch Glen						
	MG 27	MG 28	MG 5	MG 4	MG 3	MG 29	MG 31
S	1159	8564	6385	4443	1278	2128	4589
Cr	23	14	12	5	39	24	20
Co	9	12	8	ND	12	10	5
Ni	3	ND	1	ND	15	3	2
Cu	1	77	7	ND	11	12	ND
Zn	73	92	105	133	113	90	89
Ga	7	28	17	12	10	9	7
Rb	50	26	22	17	82	37	43
Sr	297	20709	9103	6924	912	2314	752
Y	32	1	2	3	15	15	11
Zr	63	38	ND	ND	43	95	41
Nb	11	ND	ND	ND	12	8	5
Ba	170	2474	1281	426	148	244	129
La	54	7	3	1	20	20	25
Pb	7	3	17	6	7	8	1
Ce	138	124	90	113	80	106	115
Th	11	5	ND	2	9	6	4

Concentrations in parts per million. ND=not detected

NA = not analysed.

Table 6.3A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Auchenreoch Glen				
	MG 30	MG 32	MG 2	MG 1	MG 105
S	996	1519	2622	1538	1465
Cr	18	14	21	16	26
Co	8	10	10	ND	8
Ni	ND	ND	3	ND	4
Cu	ND	ND	ND	3	ND
Zn	108	107	119	123	61
Ga	6	6	6	9	8
Rb	28	25	33	24	51
Sr	230	360	326	1713	318
Y	13	15	19	29	15
Zr	84	13	4	20	36
Nb	10	9	9	12	9
Ba	63	93	465	113	71
La	9	26	20	41	30
Pb	5	10	7	ND	ND
Ce	86	107	84	147	120
Th	5	5	4	3	5

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.4A: Chemical analyses of carbonate beds in the Ballagan Formation.

		Overtoun Burn					
	MG 78	MG 79	MG 80	MG 73	MG 75	MG 76	MG 77
SiO_2	6.84	9.17	18.40	15.84	9.21	10.27	19.73
Al_2O_3	3.57	2.57	3.11	4.35	2.87	3.65	3.47
TiO_2	0.07	0.09	0.08	0.15	0.09	0.14	0.08
Fe_2O_3	1.22	1.09	1.08	1.71	1.10	1.29	1.10
MnO	0.25	0.27	0.29	0.25	0.24	0.24	0.11
MgO	14.47	9.35	2.30	14.08	14.74	14.80	1.64
CaO	32.57	35.60	39.55	25.53	30.63	29.04	39.98
Na_2O	0.23	0.23	0.20	0.27	0.22	0.23	0.19
K_2O	0.60	0.63	0.74	0.96	0.72	0.86	0.87
P_2O_5	0.17	0.13	0.12	0.23	0.17	0.26	0.13
H_2O	1.29	1.06	1.50	1.58	1.24	1.11	1.48
CO_2	40.04	37.73	31.59	33.88	38.76	37.95	31.40
SO_3	0.47	1.07	0.32	0.32	0.32	0.32	-
Sr O	-	0.14	-	-	-	-	-
BaO	0.17	0.79	-	-	-	-	-
Total A	101.96	99.93	99.28	99.15	100.31	100.16	100.18
Calcite	24.24	39.89	68.65	13.40	20.50	16.67	71.36
Dolomite	61.56	42.30	2.94	58.64	62.33	64.15	-
Total B	85.80	82.19	71.59	72.04	82.83	80.82	71.36
Gypsum	0.82	1.18	0.59	0.59	0.59	0.59	-
Celestine	-	0.25	-	-	-	-	-
Barytes	0.25	1.20	-	-	-	-	-
Illite	9.25	9.71	11.39	14.78	11.07	13.24	13.26
Chlorite	2.16	-	4.09	2.22	2.25	0.76	3.73
Montmor.	2.92	1.84	-	1.48	-	2.03	-
Total C	14.33	11.55	15.48	18.48	13.32	16.03	16.99
Quartz	-	3.11	11.85	7.03	3.22	2.16	12.27
Haematite	-	-	-	-	-	-	-
Total D	101.20	99.48	99.51	98.14	99.96	99.60	100.62

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.4A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Overtoun Burn						
	MG 81	MG 102	MG 65	MG 66	MG 67	MG 68	MG 69
SiO_2	28.43	2.11	22.42	6.67	10.45	3.26	6.24
Al_2O_3	4.44	1.16	9.26	3.10	5.30	2.12	3.58
TiO_2	0.12	0.02	0.29	0.10	0.16	0.06	0.10
Fe_2O_3	1.31	0.38	3.17	1.34	1.89	0.69	1.39
MnO	0.15	0.14	0.12	0.43	0.18	0.23	0.20
MgO	1.94	2.12	3.63	15.65	9.49	14.89	15.03
CaO	34.15	49.54	30.45	31.13	33.92	33.51	31.30
Na_2O	0.21	0.18	0.25	0.22	0.26	0.21	0.20
K_2O	0.99	0.19	2.07	0.68	1.23	0.51	0.84
P_2O_5	0.17	0.08	0.15	0.16	0.20	0.17	0.16
H_2O	1.72	0.77	3.41	1.33	1.65	0.71	1.07
CO_2	26.97	40.40	24.59	39.98	36.22	42.04	40.89
SO_3	-	1.87	-	0.52	0.35	0.40	0.25
Sr O	-	0.84	-	-	-	0.07	-
BaO	-	-	-	-	-	0.13	-
Total A	100.60	99.80	99.81	101.32	101.30	99.00	101.25
Calcite	61.34	81.90	52.77	18.89	37.83	23.31	18.11
Dolomite	-	9.19	2.91	66.36	41.04	66.60	68.99
Total B	61.34	91.09	55.68	85.25	78.87	89.91	87.10
Gypsum	-	2.63	-	1.12	0.75	0.59	0.54
Celestine	-	1.49	-	-	-	0.12	-
Barytes	-	-	-	-	-	0.20	-
Illite	15.09	2.93	31.53	10.46	18.93	7.76	12.93
Chlorite	4.51	-	5.75	2.44	-	-	-
Montmor.	-	1.95	3.05	-	1.56	-	-
Total C	19.60	4.88	40.33	12.90	20.49	7.76	12.93
Quartz	19.88	-	3.33	0.94	-	-	-
Haematite	-	-	-	-	-	-	-
Total D	100.82	100.09	99.34	100.21	100.11	98.58	100.57

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.4A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Overtoun Burn					
	MG 70	MG 71	MG 72	MG 64	MG 101	MG 63
SiO_2	4.87	12.53	17.88	3.36	3.46	6.45
Al_2O_3	2.84	4.38	7.79	1.96	1.24	2.51
TiO_2	0.10	0.17	0.26	0.06	0.02	0.09
Fe_2O_3	1.43	1.40	2.50	0.89	0.40	0.84
MnO	0.24	0.21	0.12	0.27	0.11	0.31
MgO	16.55	14.90	3.48	15.08	2.14	14.82
CaO	31.62	27.10	32.68	34.67	46.76	31.32
Na_2O	0.22	0.23	0.23	0.23	0.17	0.26
K_2O	0.76	1.09	1.54	0.48	0.17	0.68
P_2O_5	0.22	0.21	0.21	0.17	0.07	0.19
H_2O	1.01	1.47	2.39	0.74	1.17	0.90
CO_2	41.01	36.24	28.81	43.10	37.93	40.12
SO_3	0.30	-	0.40	0.42	4.10	0.47
Sr O	-	-	-	-	2.99	0.18
BaO	-	-	0.21	-	-	0.12
Total A	101.20	99.93	98.50	101.43	100.73	99.23
Calcite	18.85	14.32	50.44	24.68	76.18	19.88
Dolomite	68.56	62.74	13.90	67.56	9.29	65.74
Total B	87.41	77.06	64.34	92.24	85.47	85.62
Gypsum	0.65	-	0.60	0.90	3.85	0.58
Celestine	-	-	-	-	5.30	0.32
Barytes	-	-	0.36	-	-	0.18
Illite	11.71	16.61	23.71	7.39	2.61	10.36
Chlorite	-	1.67	-	-	-	-
Montmor.	-	-	9.84	-	3.38	0.42
Total C	11.71	18.28	33.55	7.39	5.99	10.78
Quartz	-	3.82	-	-	-	0.97
Haematite	-	-	-	-	-	-
Total D	99.77	99.16	98.85	100.53	100.61	98.45

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.48: Chemical analyses of carbonate beds in the Ballagan Formation.

	Overtoun Burn						
	MG 78	MG 79	MG 80	MG 73	MG 75	MG 76	MG 77
S	1919	4304	1325	1335	1263	1298	762
Cr	15	15	22	36	21	21	36
Co	9	2	1	6	6	1	10
Ni	ND	3	1	9	1	1	ND
Cu	ND	ND	ND	65	ND	ND	ND
Zn	23	19	18	34	19	24	13
Ga	3	5	3	4	3	4	3
Rb	22	21	24	41	24	29	29
Sr	207	1213	333	239	220	216	229
Y	16	39	92	19	10	15	13
Zr	10	8	32	26	17	37	22
Nb	11	6	9	8	ND	7	10
Ba	1504	7110	159	300	131	157	196
La	23	63	181	30	17	24	28
Pb	33	65	20	7	5	2	11
Ce	99	184	372	98	43	88	77
Th	4	6	5	6	4	2	8

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.48: Chemical analyses of carbonate beds in the Ballagan Formation.

	Overtoun Burn						
	MG 81	MG 102	MG 65	MG 66	MG 67	MG 68	MG 69
S	919	7496	898	2054	1387	1632	1014
Cr	23	6	41	13	23	11	17
Co	8	12	15	4	ND	ND	3
Ni	1	ND	12	ND	4	ND	ND
Cu	ND	ND	ND	173	181	4	ND
Zn	10	13	27	20	23	12	11
Ga	4	11	14	5	6	3	3
Rb	33	103	79	111	43	16	26
Sr	412	7148	248	721	711	637	170
Y	12	16	15	23	21	12	25
Zr	17	ND	47	21	25	10	20
Nb	8	ND	8	5	9	8	9
Ba	116	242	ND	ND	123	1160	162
La	16	10	40	17	37	18	25
Pb	4	14	3	ND	1	5	ND
Ce	90	136	499	528	141	91	123
Th	8	16	10	14	8	2	7

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.48: Chemical analyses of carbonate beds in the Ballagan Formation.

	Overtoun Burn					
	MG 70	MG 71	MG 72	MG 64	MG 101	MG 63
S	1236	889	1580	1686	16363	1907
Cr	15	21	35	13	6	15
Co	3	4	12	1	ND	6
Ni	2	2	8	ND	ND	ND
Cu	ND	16	ND	ND	3	ND
Zn	15	20	28	20	56	23
Ga	4	5	10	3	5	4
Rb	26	40	60	21	13	22
Sr	183	167	493	697	25337	1452
Y	23	15	14	8	ND	12
Zr	24	64	38	20	ND	17
Nb	12	10	10	7	ND	5
Ba	213	325	2103	ND	479	1135
La	29	17	24	23	ND	11
Pb	5	1	6	ND	ND	8
Ce	111	86	106	348	100	82
Th	ND	8	7	1	ND	7

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 6.5A: Chemical analyses of carbonate beds in the Ballagen Formation.

	Gargunnock Burn, Gargunnock						
	MG 53	MG 54	MG 55	MG 56	MG 83	MG 84	MG 85
SiO_2	19.34	12.65	6.67	4.70	6.74	4.40	9.36
Al_2O_3	6.31	3.71	3.55	2.51	2.86	2.30	3.76
TiO_2	0.24	0.13	0.11	0.08	0.08	0.09	0.12
Fe_2O_3	3.21	1.66	1.30	0.84	0.93	1.14	1.39
MnO	0.16	0.17	0.19	0.24	0.24	0.31	0.20
MgO	12.34	13.22	13.96	16.10	12.57	15.27	13.65
CaO	24.77	28.38	31.92	32.51	34.22	32.41	30.53
Na_2O	0.22	0.22	0.21	0.24	0.26	0.28	0.24
K_2O	1.33	0.89	0.88	0.58	0.59	0.62	0.81
P_2O_5	0.12	0.16	0.15	0.14	0.16	0.18	0.14
H_2O	2.03	1.43	1.21	0.86	0.93	0.96	1.40
CO_2	31.22	36.25	39.49	42.45	39.75	41.80	37.56
SO_3	-	0.40	0.45	0.42	0.55	0.70	0.35
Sr O	-	-	-	-	-	0.20	-
BaO	-	-	-	-	-	-	-
Total A	101.31	99.27	100.09	101.67	99.80	100.66	99.51
Calcite	17.42	17.86	23.00	18.45	30.37	19.26	22.68
Dolomite	49.37	59.50	61.55	71.94	55.30	69.83	57.80
Total B	66.79	77.36	84.55	90.39	85.67	89.09	80.48
Gypsum	-	0.86	0.97	0.90	1.18	1.17	0.75
Celestine	-	-	-	-	-	0.35	-
Barytes	-	-	-	-	-	-	-
Illite	20.46	15.07	13.53	8.84	9.07	9.54	12.46
Chlorite	2.40	-	-	-	-	-	1.71
Montmor.	3.94	2.59	-	0.39	3.34	-	1.79
Total C	26.80	17.66	13.53	9.26	12.41	9.54	15.96
Quartz	6.02	3.49	-	-	-	-	1.60
Haematite	0.96	-	-	-	-	-	-
Total D	100.57	99.37	99.05	100.52	99.26	100.15	98.79

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.5A: Chemical analyses of carbonate beds in the Ballagan Formation

	Gargunnock Burn, Gargunnock						
	MG 86	MG 87	MG 88	MG 89	MG 57	MG 90	MG 91
SiO_2	14.02	20.77	12.42	7.18	13.33	54.23	8.51
Al_2O_3	5.43	5.63	4.07	3.65	4.27	10.95	3.00
TiO_2	0.16	0.31	0.20	0.13	0.14	0.54	0.11
Fe_2O_3	2.56	2.13	1.50	1.71	2.25	2.99	1.59
MnO	0.22	0.18	0.20	0.18	0.16	0.09	0.17
MgO	11.50	10.98	14.09	15.31	14.06	3.41	14.94
CaO	28.70	25.70	28.20	30.31	27.91	12.21	29.66
Na_2O	0.24	0.35	0.31	0.23	0.26	0.74	0.27
K_2O	0.98	1.15	0.95	0.81	0.69	1.85	0.56
P_2O_5	0.18	0.12	0.12	0.20	0.13	0.10	0.17
H_2O	1.79	2.08	1.40	1.17	1.44	2.78	1.13
CO_2	34.48	29.88	36.93	40.23	35.46	9.58	39.06
SO_3	0.30	0.30	0.30	0.37	0.37	-	0.50
Sr O	-	-	-	-	-	-	-
BaO	-	-	-	-	-	-	0.11
Total A	100.56	99.58	100.69	101.48	100.47	99.47	99.78
Calcite	23.28	23.03	15.92	15.78	18.06	21.79	15.93
Dolomite	50.80	41.39	62.71	69.76	57.66	-	67.16
Total B	74.08	64.42	78.63	85.54	75.72	21.79	83.09
Gypsum	0.65	0.65	0.65	0.80	0.80	-	0.95
Celestine	-	-	-	-	-	-	-
Barytes	-	-	-	-	-	-	0.17
Illite	15.07	17.71	14.61	12.46	10.61	28.46	8.61
Chlorite	-	4.12	-	-	3.49	7.68	-
Montmor.	11.02	1.89	3.49	1.53	3.69	7.54	6.02
Total C	26.09	23.72	18.10	13.99	17.79	43.68	14.63
Quartz	-	9.86	2.82	-	4.94	33.39	0.37
Haematite	-	-	-	-	-	-	-
Total D	100.82	98.65	100.20	100.33	99.25	98.86	99.21

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.5A: Chemical analyses of carbonate beds in the Ballagan Formation

	Gargunnock Burn, Gargunnock						
	MG 92	MG 93	MG 94	MG 95	MG 96	MG 97	MG 98
SiO_2	19.78	13.66	9.74	12.27	7.37	57.48	14.92
Al_2O_3	5.25	4.13	3.67	4.83	2.81	8.18	5.19
TiO_2	0.18	0.15	0.12	0.14	0.09	0.45	0.16
Fe_2O_3	2.75	2.15	1.75	2.19	1.95	1.82	2.92
MnO	0.16	0.16	0.17	0.16	0.17	0.10	0.15
MgO	12.70	13.92	14.30	13.89	15.43	3.64	14.51
CaO	24.75	26.76	29.72	27.44	29.91	11.92	26.36
Na_2O	0.24	0.22	0.22	0.22	0.23	0.52	0.25
K_2O	0.92	0.75	0.70	0.94	0.53	2.16	0.99
P_2O_5	0.15	0.14	0.15	0.14	0.14	0.33	0.19
H_2O	2.02	1.38	1.25	1.62	1.29	2.48	1.89
CO_2	31.41	36.06	38.21	36.42	39.21	11.53	34.47
SO_3	0.35	0.27	0.27	0.27	0.72	-	0.37
Sr O	-	-	-	-	-	-	-
BaO	-	-	-	-	0.38	-	-
Total	100.66	99.75	100.27	100.53	100.23	100.61	98.54
Calcite	16.04	12.84	18.51	14.44	16.29	15.04	14.77
Dolomite	51.04	63.73	63.00	63.00	67.15	10.30	58.61
Total B	67.08	76.57	81.51	77.44	83.44	25.34	73.38
Gypsum	0.75	0.58	0.58	0.58	1.12	-	0.80
Celestine	-	-	-	-	-	-	-
Barytes	-	-	-	-	0.58	-	-
Illite	14.17	11.53	10.78	14.46	8.17	32.58	15.70
Chlorite	3.28	-	-	-	0.46	-	3.66
Montmor.	8.07	8.24	6.83	6.28	5.31	-	2.23
Total C	25.52	19.77	17.61	20.74	13.94	32.58	21.59
Quartz	7.04	2.64	-	0.89	-	40.95	1.23
Haematite	-	-	-	-	-	-	1.24
Total D	100.39	99.56	99.70	99.65	99.08	98.87	98.24

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.5A: Chemical analyses of carbonate beds in the Ballagan Formation

	Gargunnock Burn, Gargunnock						
	MG 99	MG 58	MG 100	MG 59	MG 60	MG 61	MG 62
SiO_2	16.83	15.12	20.74	22.12	8.32	21.89	13.69
Al_2O_3	4.46	5.65	4.91	5.95	3.63	7.75	6.15
TiO_2	0.16	0.17	0.11	0.19	0.11	0.28	0.17
Fe_2O_3	1.71	2.30	2.34	2.41	1.83	3.03	2.01
MnO	0.16	0.17	0.26	0.16	0.32	0.19	0.08
MgO	6.92	12.17	7.51	3.80	13.87	8.71	1.87
CaO	32.23	27.43	30.29	31.93	30.28	25.09	40.42
Na_2O	0.27	0.26	0.22	0.23	0.23	0.27	0.19
K_2O	1.01	1.03	0.78	1.21	0.70	1.31	1.79
P_2O_5	0.18	0.13	0.16	0.18	0.13	0.16	0.15
H_2O	1.51	1.89	1.46	1.87	1.63	2.01	2.05
CO_2	32.79	33.90	30.83	28.06	38.51	28.14	31.89
SO_3	0.32	0.35	-	0.27	0.37	-	-
Sr O	-	-	-	-	-	-	-
BaO	-	-	-	-	-	-	-
Total A	98.55	100.57	99.61	98.38	99.93	98.93	100.46
Calcite	39.67	19.94	38.01	49.49	19.58	25.56	72.14
Dolomite	32.15	52.66	29.58	13.20	62.65	35.41	-
Total B	71.82	72.60	67.59	62.69	82.23	60.97	72.14
Gypsum	0.69	0.75	-	0.58	0.80	--	-
Celestine	-	-	-	-	-	-	-
Barytes	-	-	-	-	-	-	-
Illite	15.53	15.85	12.00	18.64	10.78	20.17	27.26
Chlorite	-	-	-	0.47	-	0.44	-
Montmor.	4.17	11.28	11.65	6.51	4.91	13.72	-
Total C	19.70	27.13	23.65	25.62	15.69	34.33	27.26
Quartz	6.32	-	7.30	8.41	-	2.79	-
Haematite	-	-	-	-	-	-	-
Total D	98.53	100.48	98.54	97.30	98.72	98.09	99.40

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.58: Chemical analyses of carbonate beds in the Ballagan Formation

	Gargunnock Burn, Gargunnock						
	MG 53	MG 54	MG 55	MG 56	MG 83	MG 84	MG 85
S	902	1565	1753	1714	2214	2832	1445
Cr	18	14	18	15	14	15	21
Co	3	1	ND	5	10	7	3
Ni	ND	ND	2	ND	ND	ND	1
Cu	1	ND	ND	22	ND	ND	54
Zn	36	27	31	24	27	33	20
Ga	5	3	2	3	2	4	2
Rb	21	28	28	19	20	22	27
Sr	270	257	254	236	413	1666	197
Y	53	25	25	8	15	5	14
Zr	126	65	29	26	22	ND	24
Nb	10	11	11	11	7	5	11
Ba	139	327	159	109	615	737	92
La	21	31	11	14	16	4	20
Pb	10	7	2	10	11	8	8
Ce	76	110	52	88	112	62	84
Th	7	6	3	4	7	2	4

Concentrations in parts per million. ND = not detected

NA = not analysed

Table 6.58: Chemical analyses of carbonate beds in the Ballagan Formation

	Gargunnock Burn, Gargunnock						
	MG 86	MG 87	MG 88	MG 89	MG 57	MG 90	MG 91
S	1221	1248	1177	1519	1511	468	2234
Cr	22	32	23	21	21	52	18
Co	8	7	2	3	11	ND	3
Ni	6	6	2	2	5	10	4
Cu	ND	30	13	9	161	91	63
Zn	31	28	19	25	33	24	30
Ga	7	6	4	4	5	7	3
Rb	36	280	ND	ND	25	60	23
Sr	406	243	209	251	213	111	280
Y	18	ND	17	21	21	12	13
Zr	31	202	95	26	34	90	34
Nb	10	14	10	10	7	6	11
Ba	148	336	314	298	178	381	980
La	31	27	20	23	21	18	11
Pb	4	42	ND	ND	8	7	14
Ce	106	95	81	93	95	46	70
Th	3	29	ND	ND	5	5	5

Concetrations in parts per million. ND = not detected

NA = not analysed

Table 6.58: Chemical analyses of carbonate beds in the Ballagan Formation

Gargunnock Burn, Gargunnock

	MG 92	MG 93	MG 94	MG 95	MG 96	MG 97	MG 98
S	1367	1057	1141	1113	2944	677	1503
Cr	29	27	19	23	14	53	24
Co	7	8	6	12	7	6	11
Ni	11	7	3	8	5	7	9
Cu	ND	ND	ND	29	2	40	3
Zn	34	27	24	25	27	17	36
Ga	7	5	5	4	2	3	4
Rb	35	30	24	33	19	48	33
Sr	190	237	170	185	509	137	275
Y	13	12	16	19	17	17	18
Zr	32	28	25	32	18	221	32
Nb	11	10	8	8	7	2	7
Ba	99	294	70	125	3440	434	481
La	15	16	21	24	17	24	16
Pb	4	6	11	1	ND	8	8
Ce	74	83	93	88	101	74	82
Th	8	5	5	10	4	7	4

Concentrations in parts per million. ND = not detected

NA = not analysed.

Table 658: Chemical analyses of carbonate beds in the Ballagan Formation

	Gargunnock Burn, Gargunnock						
	MG 99	MG 58	MG 100	MG 59	MG 60	MG 61	MG 62
S	1302	1447	996	1104	1473	976	585
Cr	22	29	22	26	19	34	23
Co	7	6	9	7	8	15	6
Ni	1	6	5	7	4	10	4
Cu	5	ND	ND	ND	ND	ND	ND
Zn	12	14	18	25	25	32	14
Ga	4	5	7	6	3	5	7
Rb	35	35	30	44	27	59	46
Sr	231	189	289	283	186	162	339
Y	21	15	30	22	15	19	16
Zr	74	28	22	50	25	50	45
Nb	8	9	8	10	9	10	12
Ba	294	100	100	91	399	148	62
La	38	20	39	37	14	30	15
Pb	4	ND	12	8	5	12	4
Ce	124	83	117	132	77	105	112
Th	3	5	7	6	1	6	9

Concentrations in parts per million. ND = not detected

NA = not analysed

Table 6.6A: Chemical analyses of carbonate beds in the Ballagan Formation

Little Corrie, Near Fintry

	MG174	MG175	MG176	MG177	MG178	MG179	MG180
SiO_2	13.72	24.84	23.75	12.86	37.79	33.54	19.27
Al_2O_3	5.20	3.76	7.84	3.00	8.44	12.74	6.74
TiO_2	0.20	0.13	0.25	0.06	0.28	0.49	0.21
Fe_2O_3	2.62	3.09	3.55	1.40	3.62	6.51	2.15
MnO	0.25	0.26	0.14	0.15	0.11	0.10	0.11
MgO	14.29	12.18	7.99	7.04	4.76	6.22	2.77
CaO	26.85	22.99	26.11	37.86	24.06	19.56	36.83
Na_2O	0.25	0.19	0.21	0.17	0.14	0.54	0.16
K_2O	0.86	0.22	0.46	0.17	0.43	0.31	0.63
P_2O_5	0.18	0.13	0.15	0.12	0.10	0.14	0.11
H_2O	1.84	0.79	1.68	0.63	2.74	3.42	1.36
CO_2	33.85	31.04	28.89	37.07	18.73	15.35	28.90
SO_3	0.25	0.32	-	0.50	-	-	-
SrO	-	-	-	-	-	-	-
BaO	-	0.11	-	0.23	-	-	-
Total A	100.36	100.05	101.02	101.26	101.20	98.92	99.24
Calcite	18.23	10.81	27.50	49.89	42.94	35.62	65.73
Dolomite	54.12	55.07	35.20	31.71	-	-	-
Total B	72.35	65.88	62.70	81.60	42.94	35.62	65.73
Gypsum	0.54	0.56	-	0.82	-	-	-
Celestine	-	-	-	-	-	-	-
Barytes	-	0.17	-	0.35	-	-	-
Illite	13.24	3.39	7.07	2.61	6.61	4.78	9.71
Chlorite	6.57	-	-	-	15.50	20.81	8.17
Montmor.	-	10.76	22.43	8.65	4.86	14.55	6.01
Total C	19.81	14.15	29.50	11.26	26.97	40.14	23.89
Quartz	5.72	15.98	5.28	5.79	27.92	16.97	8.67
Haematite	1.16	2.72	2.77	1.11	2.89	5.98	1.08
Total D	99.58	99.46	100.25	100.93	100.72	98.00	99.37

Totals: A-Analysis B Carbonate C-Clay and D-Computed Minerals

Table 6.6A: Chemical analyses of carbonate beds in the Ballagan Formation Little Corrie, Near Fintry

	MG181	MG182	MG183	MG184	MG185	MG186	MG187
SiO_2	8.58	11.58	12.05	15.17	21.71	15.32	19.62
Al_2O_3	3.12	4.24	5.02	6.44	4.98	6.65	6.76
TiO_2	0.12	0.14	0.17	0.24	0.16	0.19	0.23
Fe_2O_3	1.60	3.22	2.5',	3.36	3.39	4.44	3.82
MnO	0.24	0.23	0.22	0.25	0.22	0.21	0.26
MgO	12.40	14.14	12.89	12.71	12.86	12.97	11.82
CaO	33.08	28.51	29.40	26.45	23.58	25.91	24.45
Na_2O	0.20	0.37	0.25	0.35	0.32	0.29	0.41
K_2O	0.51	0.51	0.62	0.57	0.34	0.48	0.53
P_2O_5	0.18	0.20	0.18	0.21	0.13	0.20	0.23
H_2O	1.02	1.57	1.51	1.47	1.23	1.97	1.85
CO_2	38.07	35.31	35.38	33.83	32.12	31.61	29.85
SO_3	0.42	0.27	-	0.27	0.50	-	0.32
Sr O	-	-	-	-	-	-	-
BaO	-	-	-	-	0.33	-	-
Total A	99.54	100.29	100.23	101.32	98.78	100.24	100.17
Calcite	30.45	20.79	24.48	16.80	10.30	20.60	18.59
Dolomite	51.71	54.83	51.57	55.40	57.81	47.25	45.42
Total B	82.16	75.62	76.05	72.20	68.11	67.85	64.01
Gypsum	0.90	0.58	-	0.58	0.71	-	0.69
Celestine	-	-	-	-	-	-	-
Barytes	-	-	-	-	0.50	-	-
Illite	7.85	7.85	9.54	8.78	5.25	7.39	8.17
Chlorite	2.65	6.30	4.20	-	-	8.05	5.36
Montmor.	1.74	0.97	5.19	16.20	13.68	7.57	10.86
Total C	12.24	15.12	18.93	24.98	18.93	23.01	24.39
Quartz	2.94	5.67	2.94	-	6.89	4.86	7.15
Haematite	0.73	2.35	1.49	2.39	2.81	3.63	2.94
Total D	98.97	99.34	99.41	100.15	97.95	99.35	99.18

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.6A: Chemical analyses of carbonate beds in the Ballagan Formation Little Corrie, Near Fintry

	MG188	MG189
SiO_2	3.51	27.45
Al_2O_3	1.66	9.75
TiO_2	0.03	0.37
Fe_2O_3	0.74	5.41
MnO	0.13	0.18
MgO	4.19	9.16
CaO	48.19	20.21
Na_2O	0.24	0.24
K_2O	0.16	0.54
P_2O_5	0.13	0.16
H_2O	0.39	2.08
CO_2	40.91	25.23
SO_3	0.70	-
Sr O	-	-
BaO	-	-
Total A	100.98	100.78
Calcite	77.23	14.76
Dolomite	14.57	39.26
Total B	91.80	54.02
Gypsum	1.50	-
Celestine	-	-
Barytes	-	-
Illite	2.46	8.32
Chlorite	3.12	0.79
Montmor.	-	27.22
Total C	5.58	36.33
Quartz	1.61	4.98
Haematite	0.47	4.49
Total D	100.96	99.82

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals

Table 6.68: Chemical analyses of carbonate beds in the Ballagan Formation

Little Corrie, Near Fintry

	MG 174	MG 175	MG 176	MG 177	MG 178	MG 179	MG 180
S	1048	1326	831	1999	597	679	501
Cr	NA	NA	NA	NA	NA	NA	NA
Co	NA	NA	NA	NA	NA	NA	NA
Ni	NA	NA	NA	NA	NA	NA	NA
Cu	ND	ND	ND	ND	ND	2	ND
Zn	21	25	38	13	31	52	20
Ga	5	5	11	3	11	15	6
Rb	NA	NA	NA	NA	NA	NA	NA
Sr	185	274	319	515	178	192	173
Y	NA	NA	NA	NA	NA	NA	NA
Zr	NA	NA	NA	NA	NA	NA	NA
Nb	NA	NA	NA	NA	NA	NA	NA
Ba	99	1033	393	2109	117	238	24
La	NA	NA	NA	NA	NA	NA	NA
Pb	NA	NA	NA	NA	NA	NA	NA
Ce	105	63	134	103	97	81	134
Tg	NA	NA	NA	NA	NA	NA	NA

Concentrations in parts per million. ND = not detected

NA = not analysed

Table 6.68: Chemical analyses of carbonate beds in the Ballagan Formation

Little Corrie, Near Fintry

	MG 181	MG 182	MG 183	MG 184	MG 185	MG 186	MG 187
S	1661	1110	937	1060	1959	877	1242
Cr	NA	NA	NA	NA	NA	NA	NA
Co	NA	NA	NA	NA	NA	NA	NA
Ni	NA	NA	NA	NA	NA	NA	NA
Cu	ND	ND	ND	2	ND	2	ND
Zn	29	25	26	26	32	34	33
Ga	3	3	8	12	6	8	6
Rb	NA	NA	NA	NA	NA	NA	NA
Sr	340	170	159	200	329	150	201
Y	NA	NA	NA	NA	NA	NA	NA
Zr	NA	NA	NA	NA	NA	NA	NA
Nb	NA	NA	NA	NA	NA	NA	NA
Ba	NA	NA	NA	753	2985	301	298
La	NA	NA	NA	NA	NA	NA	NA
Pb	NA	NA	NA	NA	NA	NA	NA
Ce	NA	NA	NA	70	88	82	150
Th	NA	NA	NA	NA	NA	NA	NA

Concentrations in parts per million. ND = not detected

NA = not analysed

Table 6.68: Chemical analyses of carbonate beds in the Ballagan Formation

	Little Corrie, Near Fintry	
	MG 188	MG 189
S	2804	729
Cr	NA	NA
Co	NA	NA
Ni	NA	NA
Cu	ND	ND
Zn	2	44
Ga	0	11
Rb	NA	NA
Sr	267	179
Y	NA	NA
Zr	NA	NA
Nb	NA	NA
Ba	37	276
La	NA	NA
Pb	NA	NA
Ce	180	30
Th	NA	NA

Concentrations in parts per million. ND = not detected

NA = not analysed

Table 6.7A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Ballagan Glen						
	MG156	MG157	MG159	MG160	MG162	MG163	MG165
SiO_2	11.37	6.06	20.94	12.93	7.66	9.05	9.66
Al_2O_3	4.43	2.57	7.61	5.49	3.25	3.84	4.10
TiO_2	0.17	0.09	0.27	0.20	0.12	0.13	0.15
Fe_2O_3	2.19	1.61	3.66	5.74	4.51	3.77	2.53
MnO	0.20	0.29	0.19	0.27	0.32	0.24	0.23
MgO	12.33	15.32	11.44	10.83	13.54	12.41	13.20
CaO	30.32	31.24	23.47	29.25	31.75	30.76	29.97
Na_2O	0.39	0.28	0.17	0.24	0.20	0.16	0.37
K_2O	0.49	0.35	0.59	0.56	0.10	0.50	0.40
P_2O_5	0.17	0.18	0.17	0.19	0.16	0.17	0.16
H_2O	1.47	0.84	1.98	1.41	1.29	0.97	1.05
CO_2	35.57	40.77	29.06	34.24	36.92	37.33	37.53
SO_3	0.37	0.95	-	0.27	0.32	-	0.27
Sr O	-	0.70	-	-	-	-	0.08
BaO	-	-	-	-	-	-	-
Total A	99.47	101.25	99.55	101.62	100.14	99.33	99.70
Calcite	26.41	17.77	17.69	25.87	28.57	24.90	21.11
Dolomite	50.20	69.05	44.59	47.91	51.04	55.27	59.19
Total B	76.61	86.82	62.28	73.78	79.61	80.17	80.30
Gypsum	0.80	0.88	-	0.58	0.69	-	0.45
Celestine	-	1.24	-	-	-	-	0.14
Barytes	-	-	-	-	-	-	-
Illite	7.54	5.39	9.07	8.61	1.54	7.71	6.17
Chlorite	3.60	-	4.54	-	8.00	-	-
Montmor.	5.39	5.06	14.26	12.97	-	7.82	9.88
Total C	16.53	10.45	27.87	21.58	9.54	15.53	16.05
Quartz	3.25	-	5.94	-	5.17	-	-
Haematite	1.34	1.02	2.66	4.79	4.34	2.82	1.69
Total D	98.53	100.41	98.75	100.73	99.35	98.62	98.63

Totals: A-Analyses B-Carbonate C-Clay and D-Computed Minerals.

Table 6.7A: Chemical analyses of carbonate beds in the Ballagan Formation.

	Ballagan Glen					
	MG166	MG167	MG170	MG171	MG172	MG173
SiO_2	9.66	7.39	9.13	26.19	5.04	20.91
Al_2O_3	4.10	3.79	2.65	3.48	1.40	9.87
TiO_2	0.15	0.11	0.08	0.11	0.03	0.37
Fe_2O_3	2.41	2.00	1.55	1.67	3.24	6.11
MnO	0.24	0.18	0.13	0.13	0.13	0.13
MgO	13.71	14.55	13.89	11.53	14.53	12.12
CaO	30.54	30.80	31.52	24.02	33.26	19.81
Na_2O	0.13	0.15	0.16	0.19	0.16	0.21
K_2O	0.48	0.49	0.35	0.28	0.15	1.14
P_2O_5	0.13	0.14	0.13	0.14	0.05	0.15
H_2O	1.00	0.95	0.85	0.92	0.41	2.57
CO_2	38.39	39.59	39.43	31.06	41.71	27.12
SO_3	-	0.30	0.40	0.32	0.32	-
Sr O	-	-	-	-	0.19	-
BaO	-	-	-	-	-	-
Total A	100.94	100.44	100.27	100.04	100.62	100.51
Calcite	21.71	19.15	21.84	14.30	23.43	9.04
Dolomite	60.44	65.30	62.50	51.90	65.81	48.50
Total B	82.15	84.45	84.34	66.20	89.24	57.54
Gypsum	-	0.65	0.86	0.69	0.37	-
Celestine	-	-	-	-	0.34	-
Barytes	-	-	-	-	-	-
Illite	7.39	6.93	5.39	4.32	2.32	17.53
Chlorite	-	-	-	-	-	2.72
Montmor.	8.98	5.91	5.35	9.08	3.22	18.28
Total C	16.37	12.84	10.74	13.40	5.54	38.53
Quartz	-	-	2.88	17.99	1.74	-
Haematite	1.60	1.24	0.96	1.19	2.98	4.18
Total D	100.12	99.18	99.78	99.47	100.21	100.25

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.78: Chemical analyses of carbonate beds in the Ballagan Formation

	Ballagan Glen						
	MG 156	MG 157	MG 159	MG 160	MG 162	MG 163	MG 165
S	1524	3773	789	1086	1349	769	1051
Cr	NA	NA	NA	NA	NA	NA	NA
Co	NA	NA	NA	NA	NA	NA	NA
Ni	NA	NA	NA	NA	NA	NA	NA
Cu	ND	2	ND	ND	ND	ND	ND
Zn	27	31	28	20	28	21	26
Ga	3	3	6	6	3	4	6
Rb	NA	NA	NA	NA	NA	NA	NA
Sr	165	5916	247	242	314	314	735
Y	NA	NA	NA	NA	NA	NA	NA
Zr	NA	NA	NA	NA	NA	NA	NA
Nb	NA	NA	NA	NA	NA	NA	NA
Ba	158	910	141	63	457	45	151
La	NA	NA	NA	NA	NA	NA	NA
Pb	NA	NA	NA	NA	NA	NA	NA
Ce	79	79	64	93	82	113	98
Th	NA	NA	NA	NA	NA	NA	NA

Concentrations in parts per million ND = not detected

NA = not analysed

Table 6.78: Chemical analyses of carbonate beds in the Ballagan Formation

	Ballagan Glen					
	MG 166	MG 167	MG 170	MG 171	MG 172	MG 173
S	898	1164	1606	1298	1292	700
Cr	NA	NA	NA	NA	NA	NA
Co	NA	NA	NA	NA	NA	NA
Ni	NA	NA	NA	NA	NA	NA
Cu	ND	ND	10	31	ND	ND
Zn	17	20	26	19	35	41
Ga	4	3	1	4	2	10
Rb	NA	NA	NA	NA	NA	NA
Sr	297	510	308	262	1558	440
Y	NA	NA	NA	NA	NA	NA
Zr	NA	NA	NA	NA	NA	NA
Nb	NA	NA	NA	NA	NA	NA
Ba	136	193	40	355	190	99
La	NA	NA	NA	NA	NA	NA
Pb	NA	NA	NA	NA	NA	NA
Ce	96	91	69	46	73	83
Th	NA	NA	NA	NA	NA	NA

Concentrations in parts per million. ND = not detected

NA = not analysed

Table 6.8A: Chemical analyses of a carbonate nodule in the Ballagan Formation.

	Overtoun Burn						
	MG N1	MG N2	MG N3	MG N4	MG N5	MG N6	MG N7
SiO_2	5.05	5.02	5.25	5.27	5.68	4.87	5.07
Al_2O_3	2.74	2.76	2.89	2.86	2.89	2.68	2.71
TiO_2	0.09	0.09	0.10	0.10	0.10	0.08	0.09
Fe_2O_3	1.05	1.06	1.06	1.09	1.13	1.04	1.05
MnO	0.38	0.38	0.38	0.37	0.40	0.39	0.38
MgO	15.60	15.50	15.22	15.49	15.16	14.91	15.03
CaO	31.93	31.95	31.82	31.87	31.85	32.67	32.41
Na_2O	0.25	0.26	0.24	0.28	0.31	0.27	0.28
K_2O	0.69	0.69	0.71	0.73	0.73	0.68	0.69
P_2O_5	0.16	0.16	0.17	0.17	0.18	0.17	0.17
H_2O	0.79	0.79	0.79	0.84	0.84	0.84	0.84
CO_2	40.93	41.15	40.74	41.47	40.71	41.07	41.00
SO_3	0.32	0.32	0.32	0.35	0.39	0.35	0.35
Sr O	-	-	-	-	-	-	-
BaO	-	-	-	-	-	-	-
Total A	99.98	100.13	99.69	100.89	100.37	100.02	100.07
Calcite	20.09			18.57			
Dolomite	67.25			69.78			
Total B	87.34			88.35			
Gypsum	0.69			0.75			
Celestine	-			-			
Barytes	-			-			
Illite	10.61			11.25			
Chlorite	-			-			
Montmor.	-			-			
Total C	10.61			11,25			
Quartz	-			-			
Haematite	-			-			
Total D	98.64			100.35			

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.8A: Chemical analyses of a carbonate nodule in the Ballagan Formation.

	Overtoun Burn			
	MG N8	MG N9	MG N10	MG N11
SiO_2	4.83	4.78	4.79	5.14
Al_2O_3	2.70	2.67	2.73	2.80
TiO_2	0.09	0.08	0.09	0.10
Fe_2O_3	1.05	1.03	1.04	1.08
MnO	0.38	0.40	0.39	0.38
MgO	15.36	15.38	15.50	14.83
CaO	32.25	32.44	32.07	32.34
Na_2O	0.19	0.26	0.23	0.29
K_2O	0.69	0.66	0.70	0.69
P_2O_5	0.16	0.17	0.17	0.17
H_2O	0.79	0.79	0.79	0.79
CO_2	40.89	41.41	41.25	41.08
SO_3	0.32	0.36	0.32	0.36
Sr O	-			-
BaO	-			-
Total A	99.70	100.43	100.07	100.05
Calcite	21.32			21.14
Dolomite	66.03			66.60
Total B	87.35			87.74
Gypsum	0.69			0.75
Celestine	-			-
Barytes	-			-
Illite	10.61			10.61
Chlorite	-			-
Montmor.	-			-
Total C	10.61			10.61
Quartz	-			-
Haematite	-			-
Total D	98.65			99.10

Totals: A-Analysis B-Carbonate C-Clay and D-Computed Minerals.

Table 6.8B: Chemical analyses of a carbonate nodule in the Ballagan Formation.

	Overtoun Burn				
	MG N1	MG N4	MG N5	MG N8	MG N11
S	1252	1356	1549	1262	1440
Cr	16	17	15	19	15
Co	10	8	5	12	9
Ni	ND	ND	ND	ND	ND
Cu	ND	ND	ND	ND	ND
Zn	20	24	19	22	21
Ga	2	4	3	1	3
Rb	NA	NA	NA	NA	NA
Sr	166	204	195	175	194
Y	NA	NA	NA	NA	NA
Zr	21	25	21	19	22
Nb	9	12	8	8	12
Ba	1	ND	11	7	51
La	18	9	27	22	23
Pb	NA	NA	NA	NA	NA
Ce	NA	NA	NA	NA	NA
Th	NA	NA	NA	NA	NA

Concentrations in parts per million. ND = not detected

NA = not analysed.

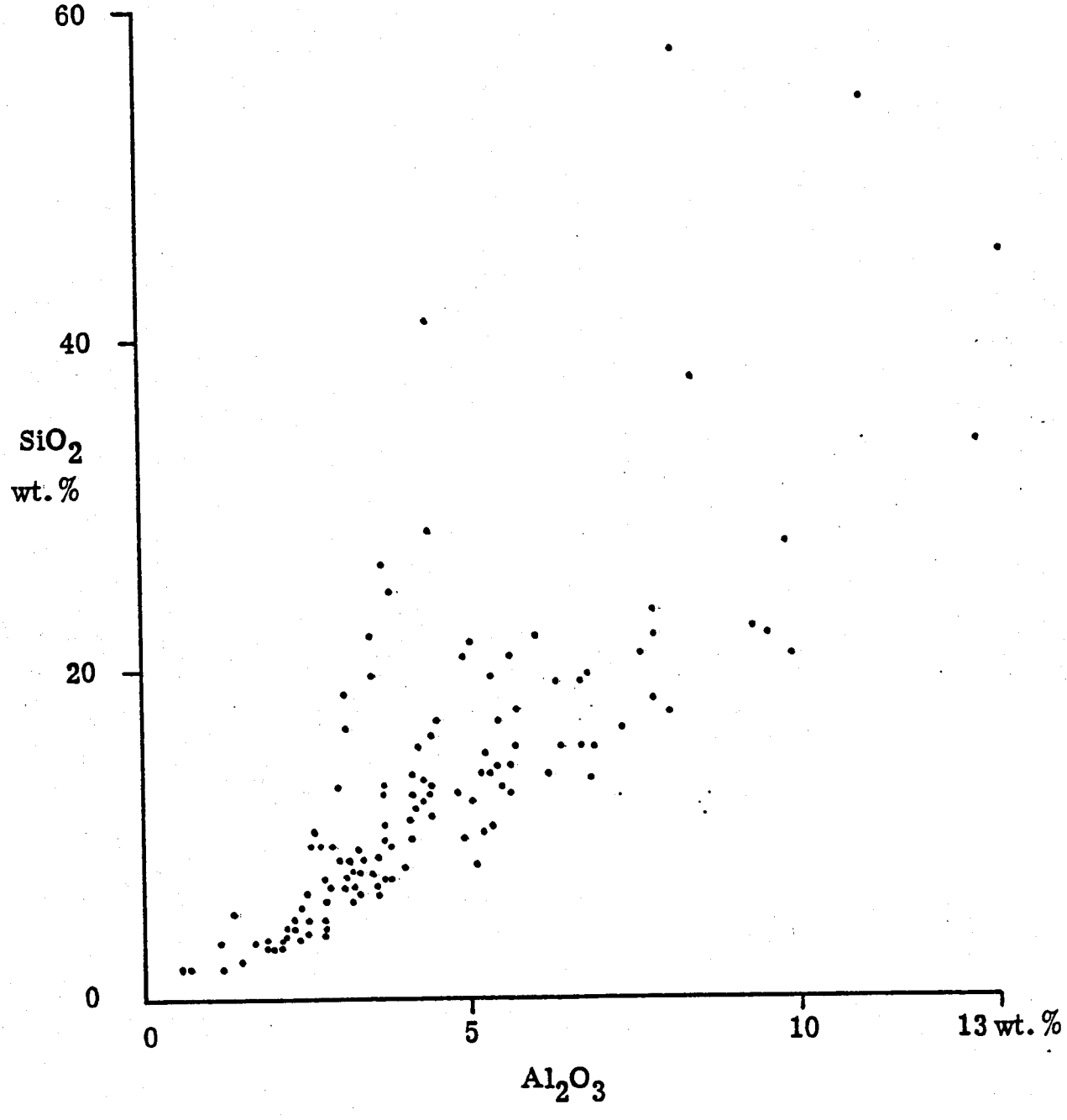


Fig. 6.1 : Plots of Al_2O_3 against SiO_2 wt. %

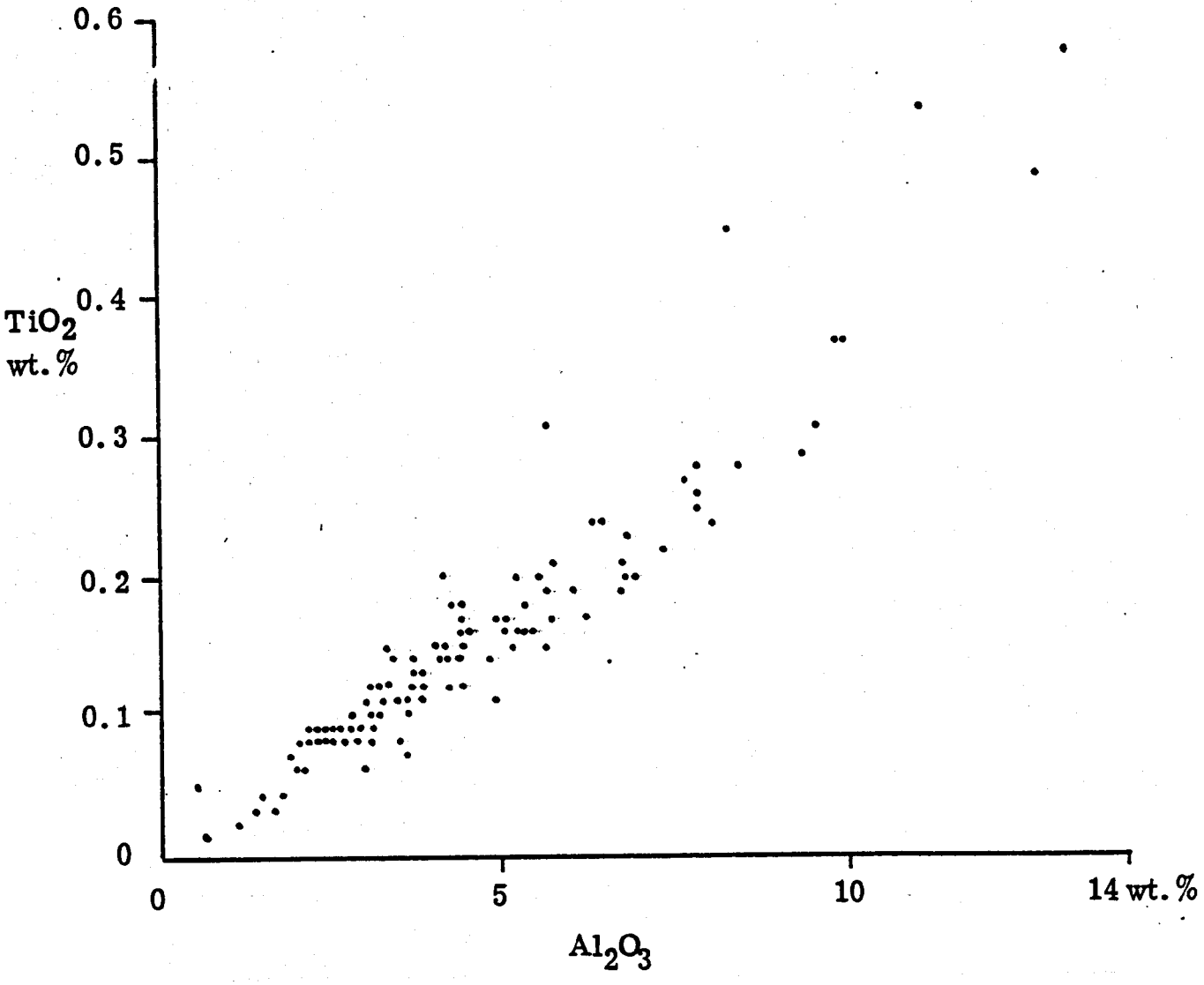


Fig. 6.2.: Plots of Al_2O_3 wt.% against TiO_2 wt.%

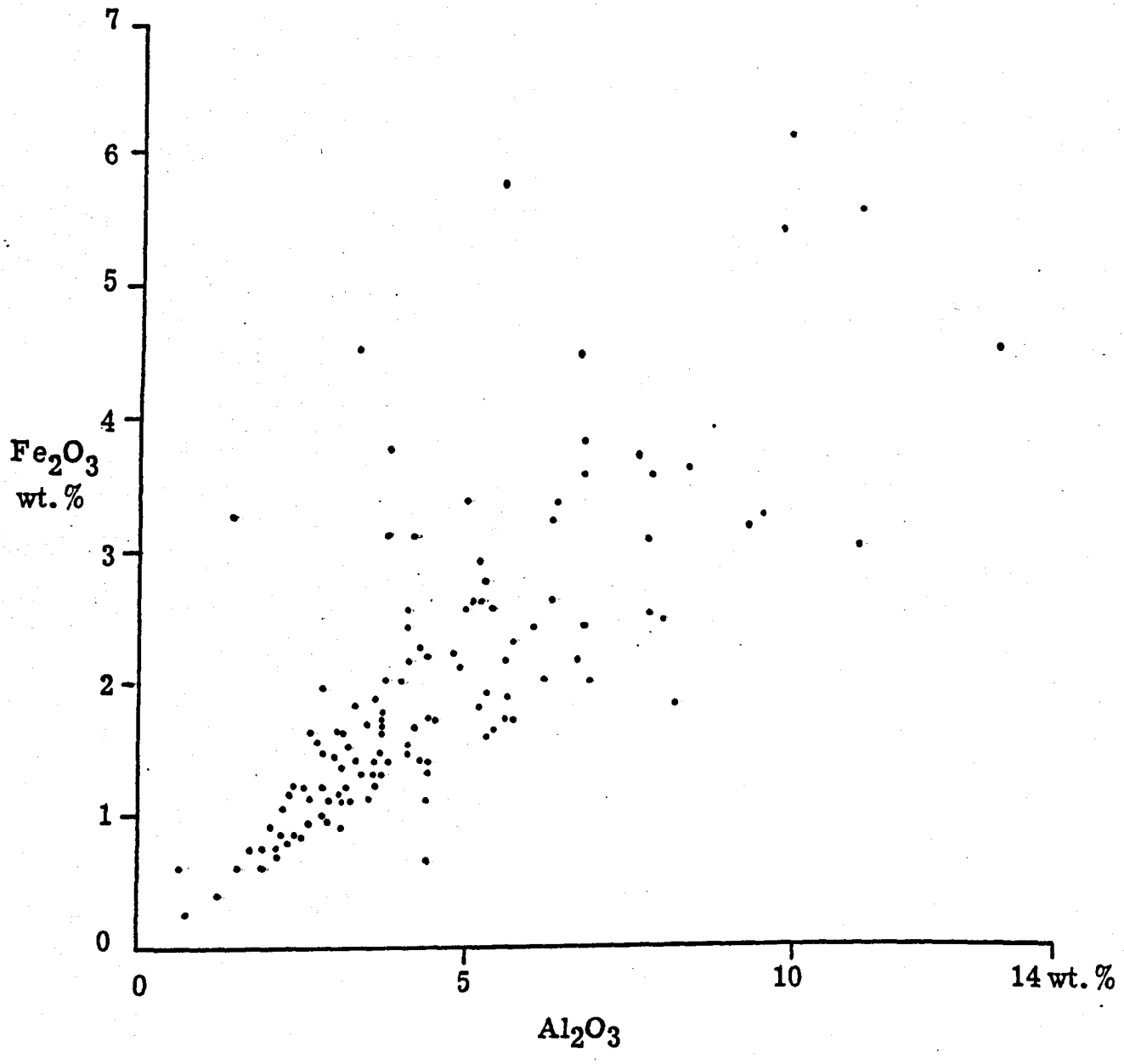


Fig. 6.3 : Plots of Al_2O_3 wt. % against Fe_2O_3 wt. %

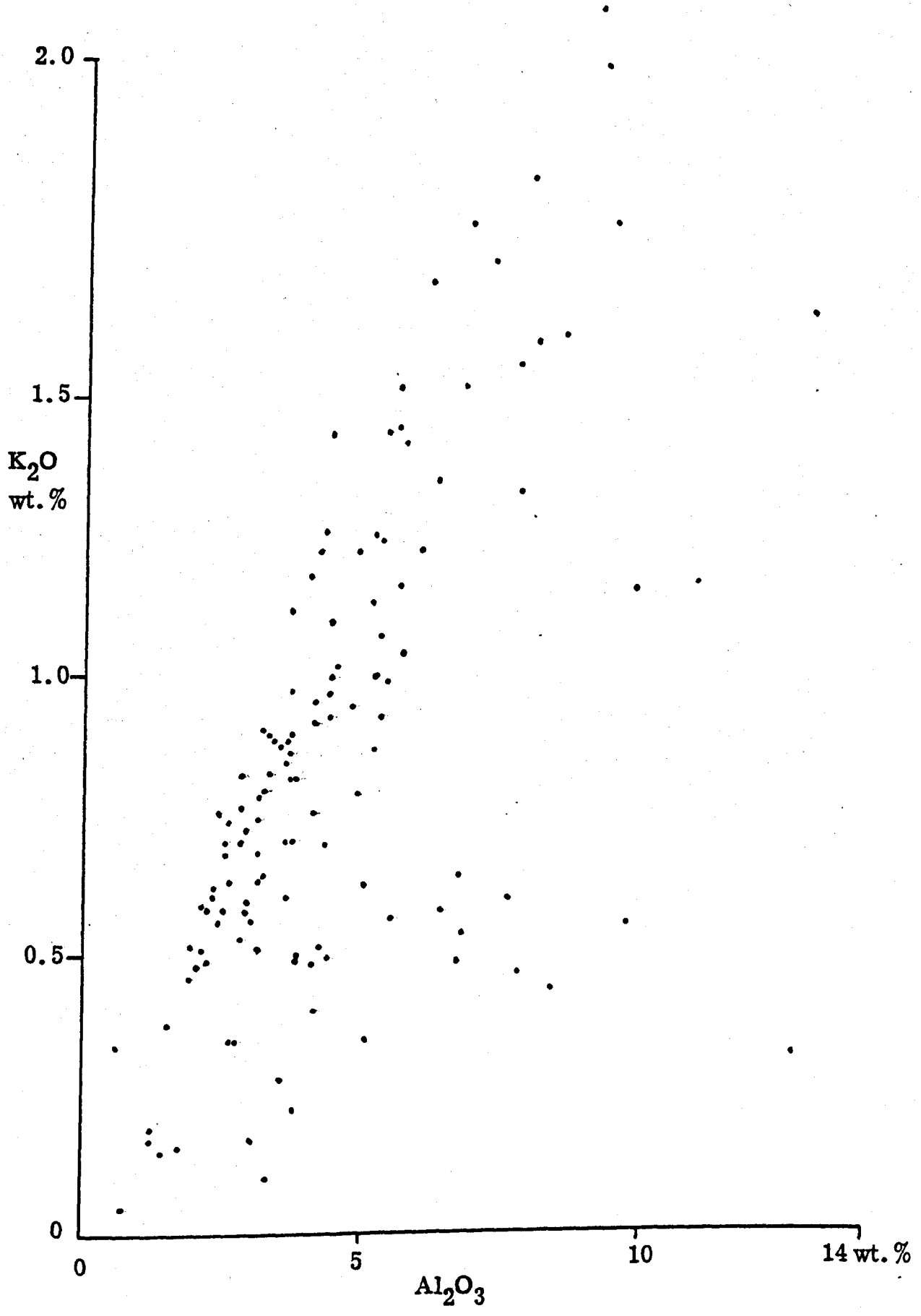


Fig. 6.4 : Plots of Al_2O_3 wt.% against K_2O wt.%.

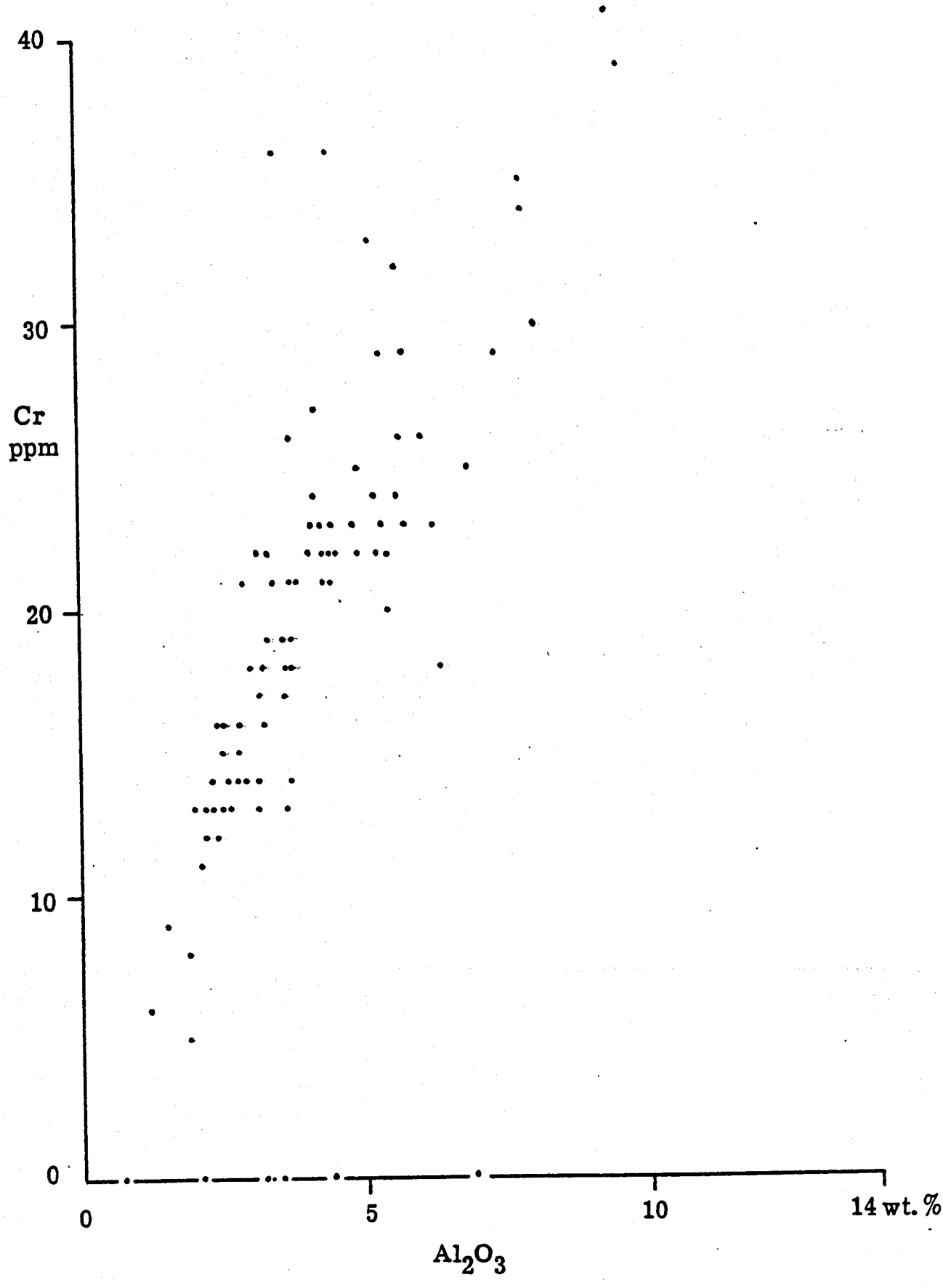


Fig. 6.5 : Plots of Al_2O_3 wt. % against Cr. ppm

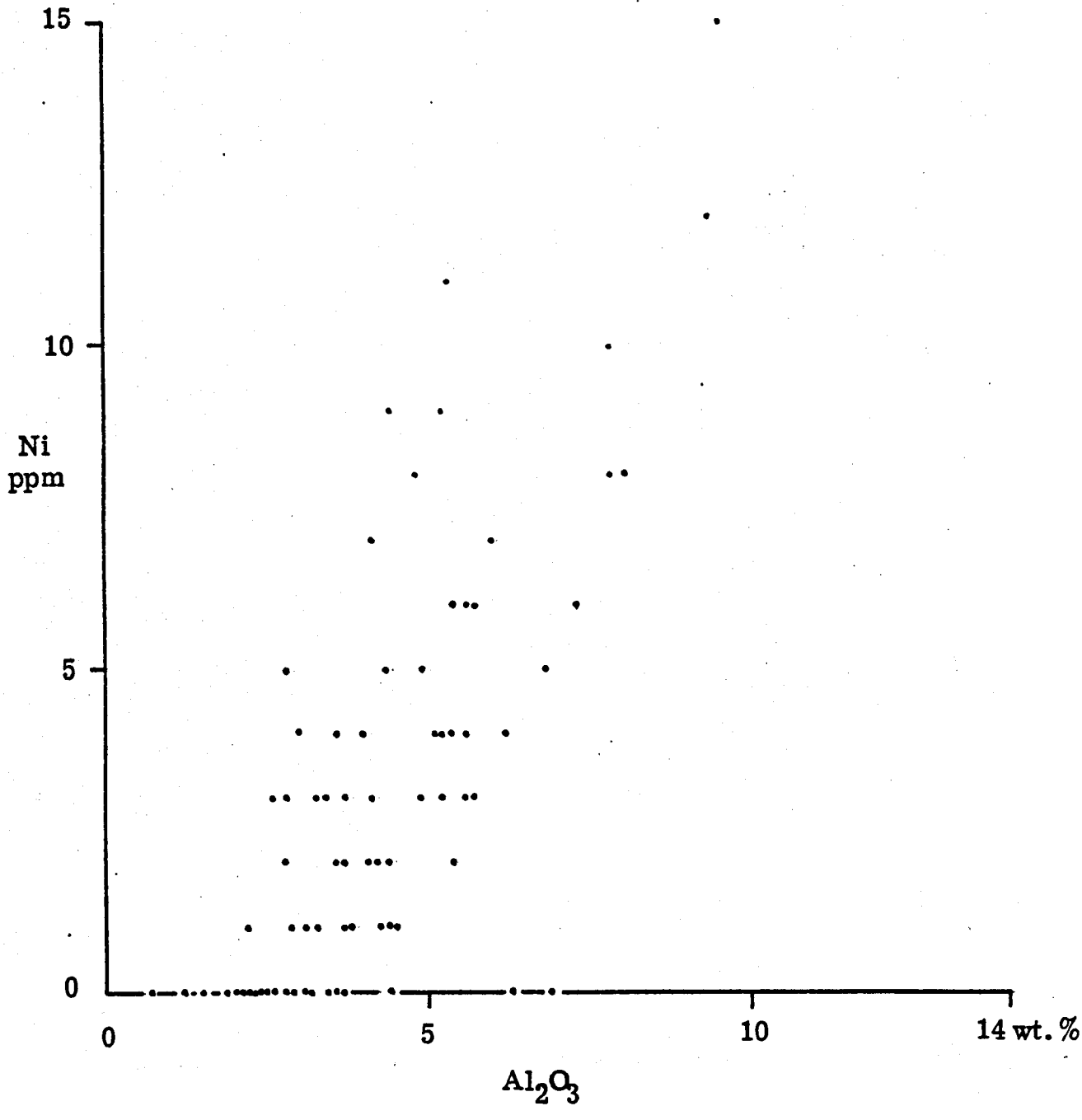


Fig. 6.6 : Plots of Al_2O_3 wt. % against Ni. ppm

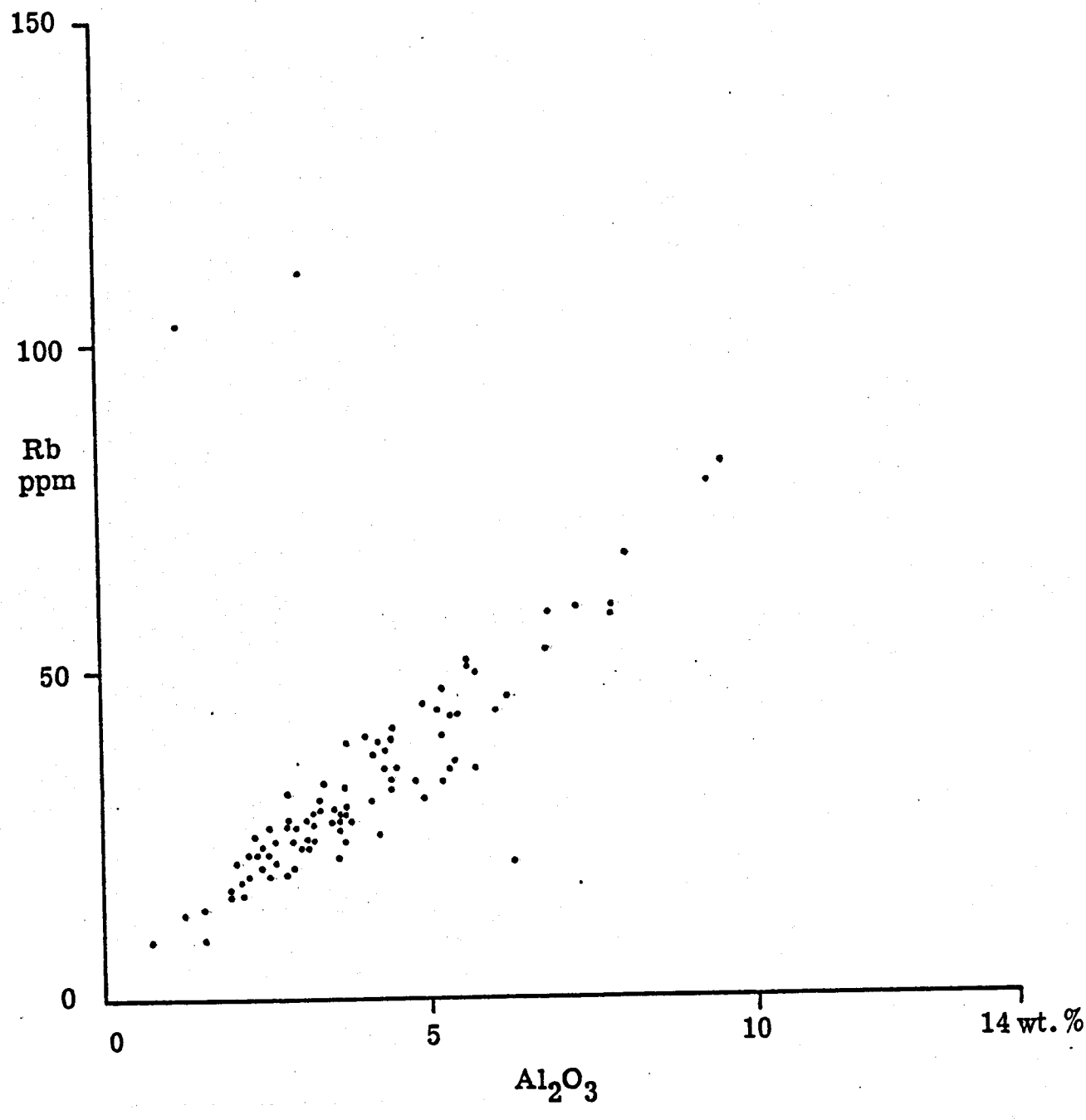


Fig. 6.7 : Plots of Al_2O_3 wt. % against Rb. ppm

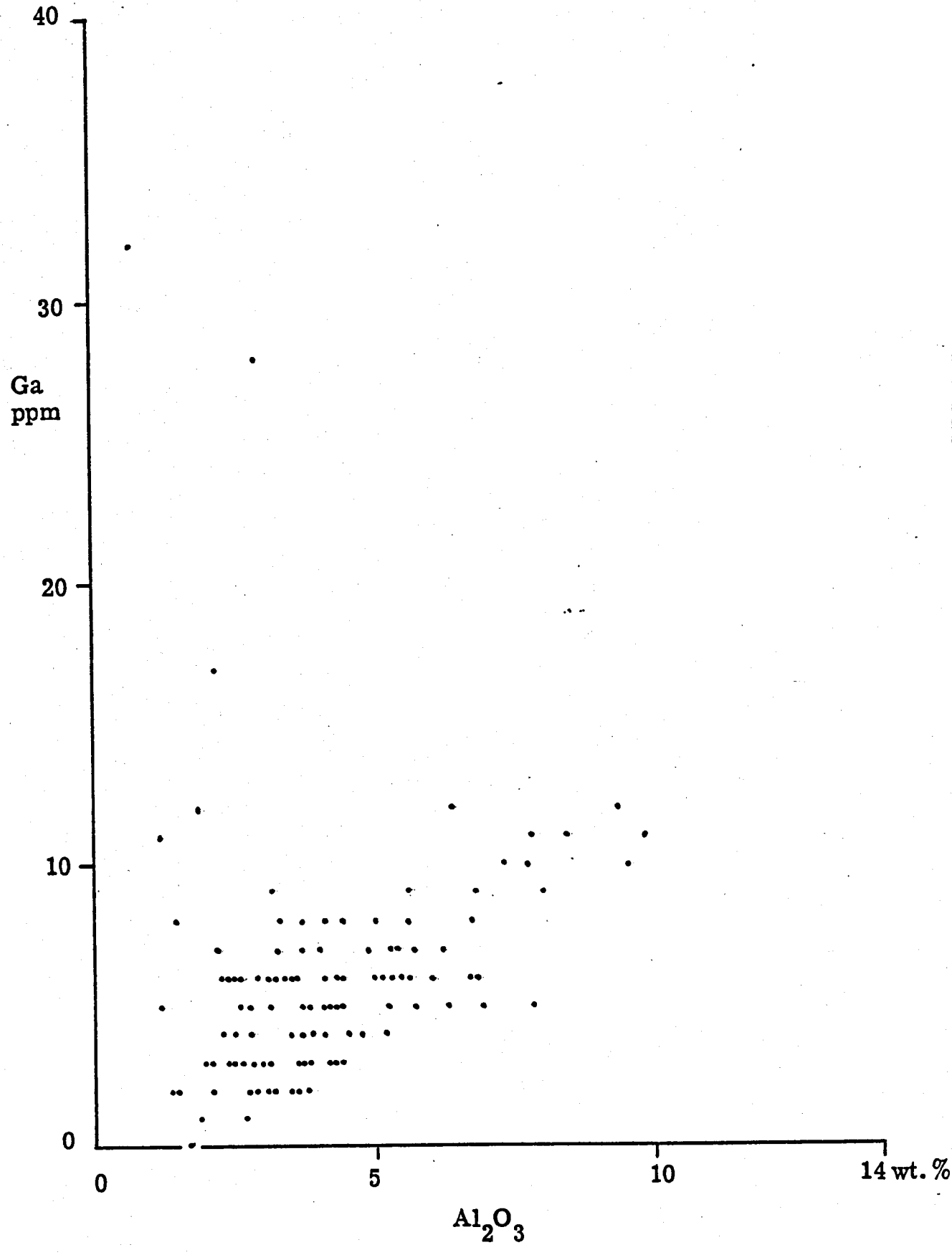


Fig. 6.8 : Plots of Al_2O_3wt. % against Ga. ppm

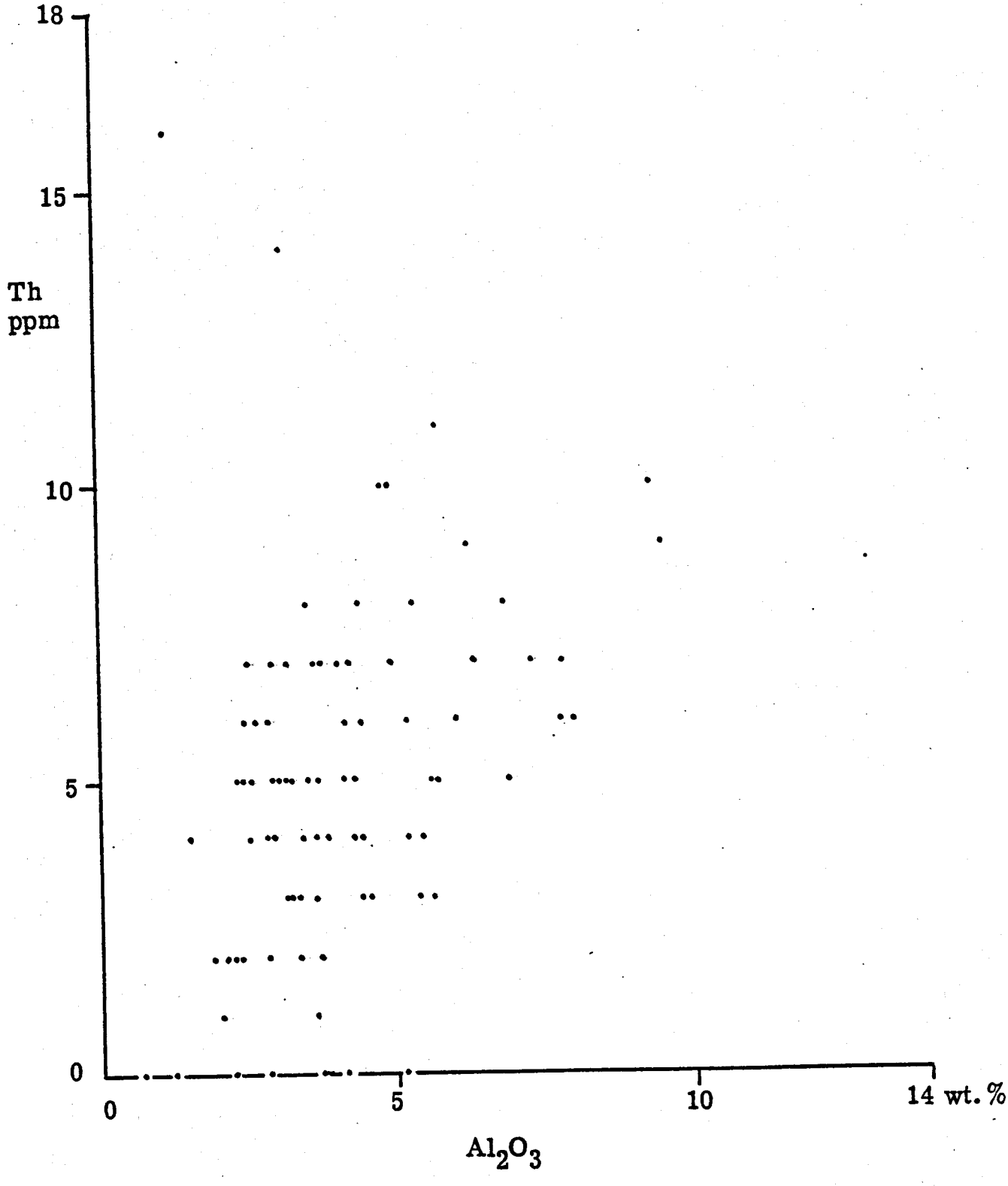


Fig. 6.9. : Plots of Al_2O_3 wt. % against Th. ppm

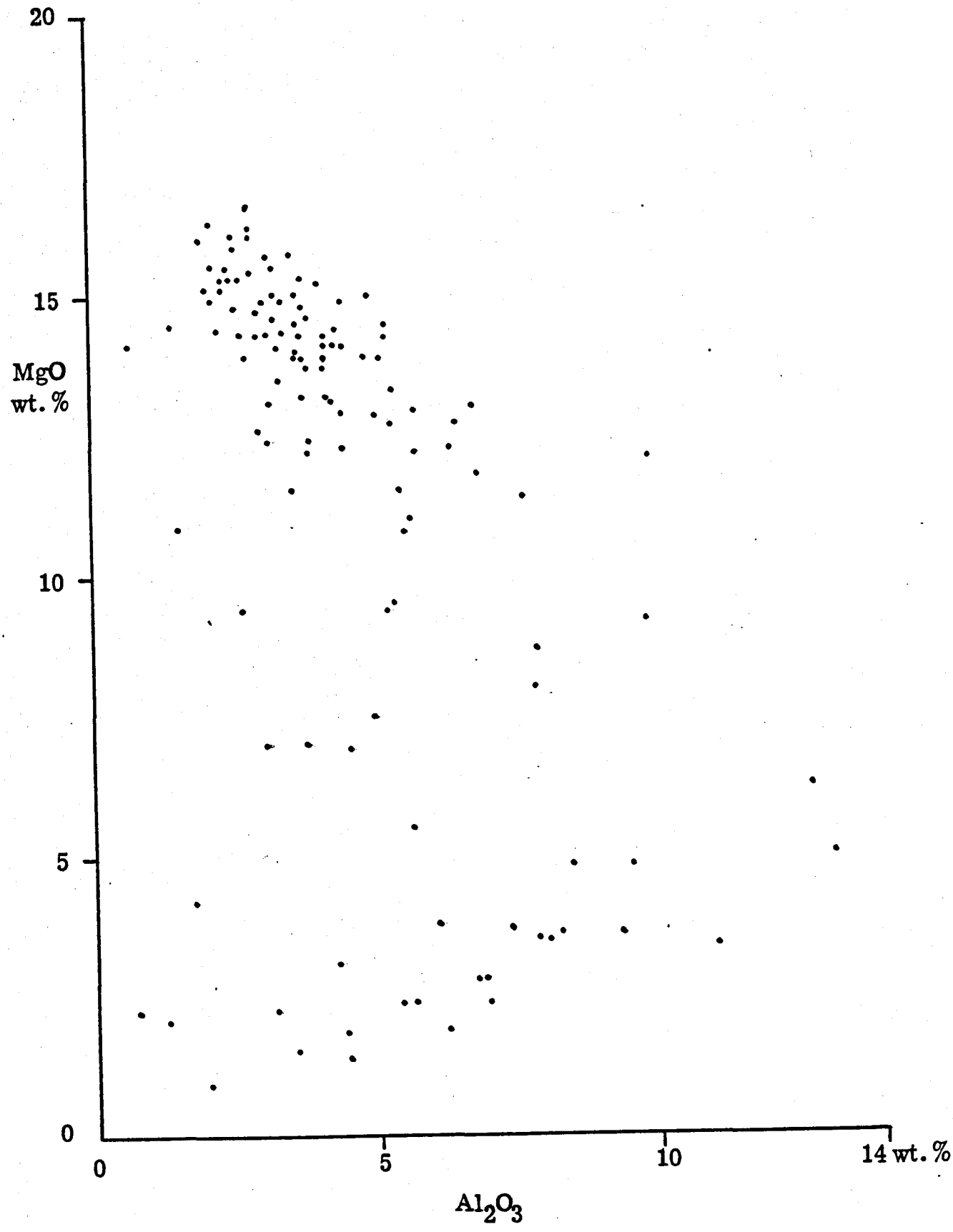


Fig. 6.10 : Plots of Al_2O_3 wt. % against MgO wt. %

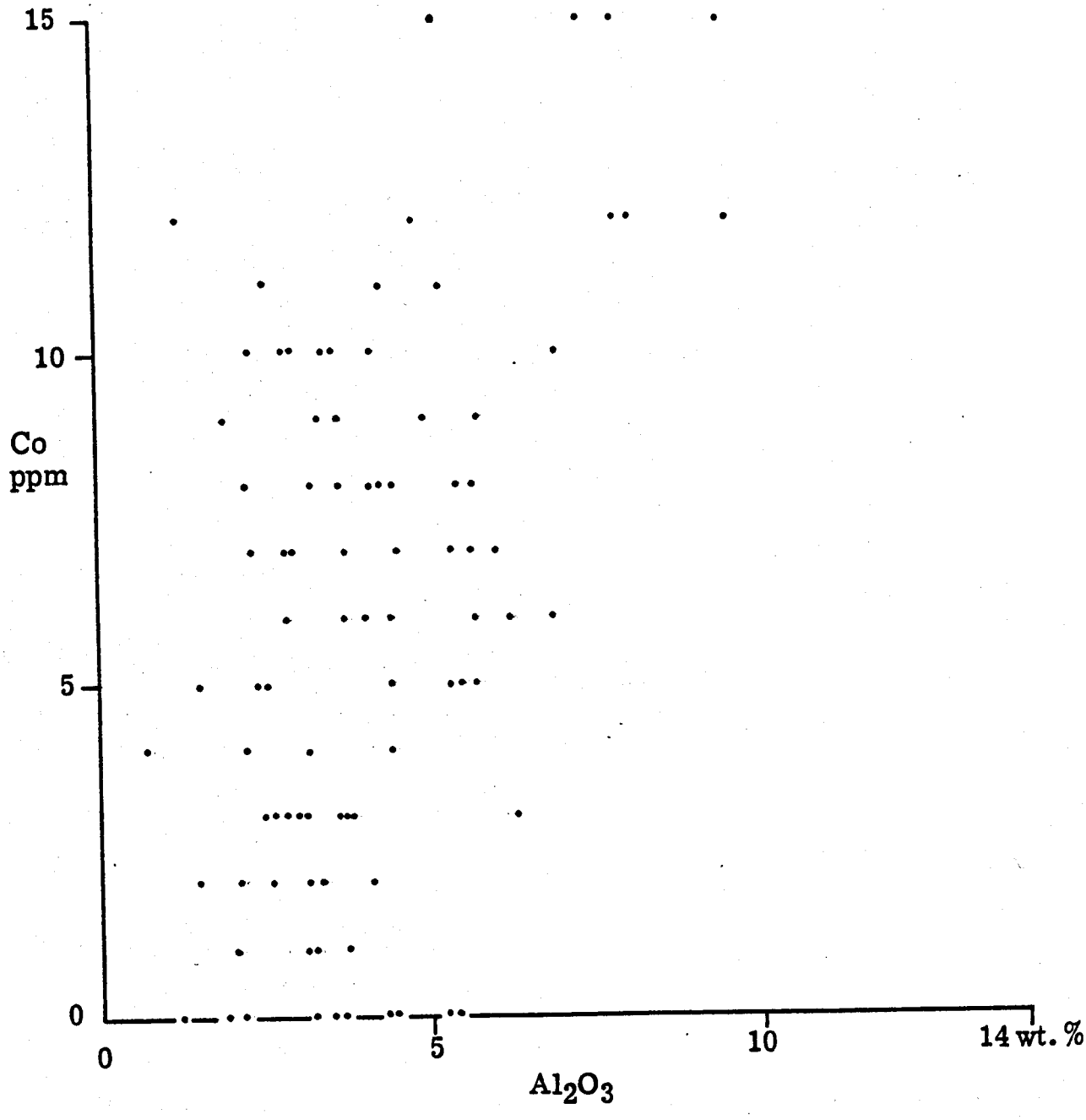


Fig. 6.11 : Plots of Al_2O_3 wt. % against Co. ppm

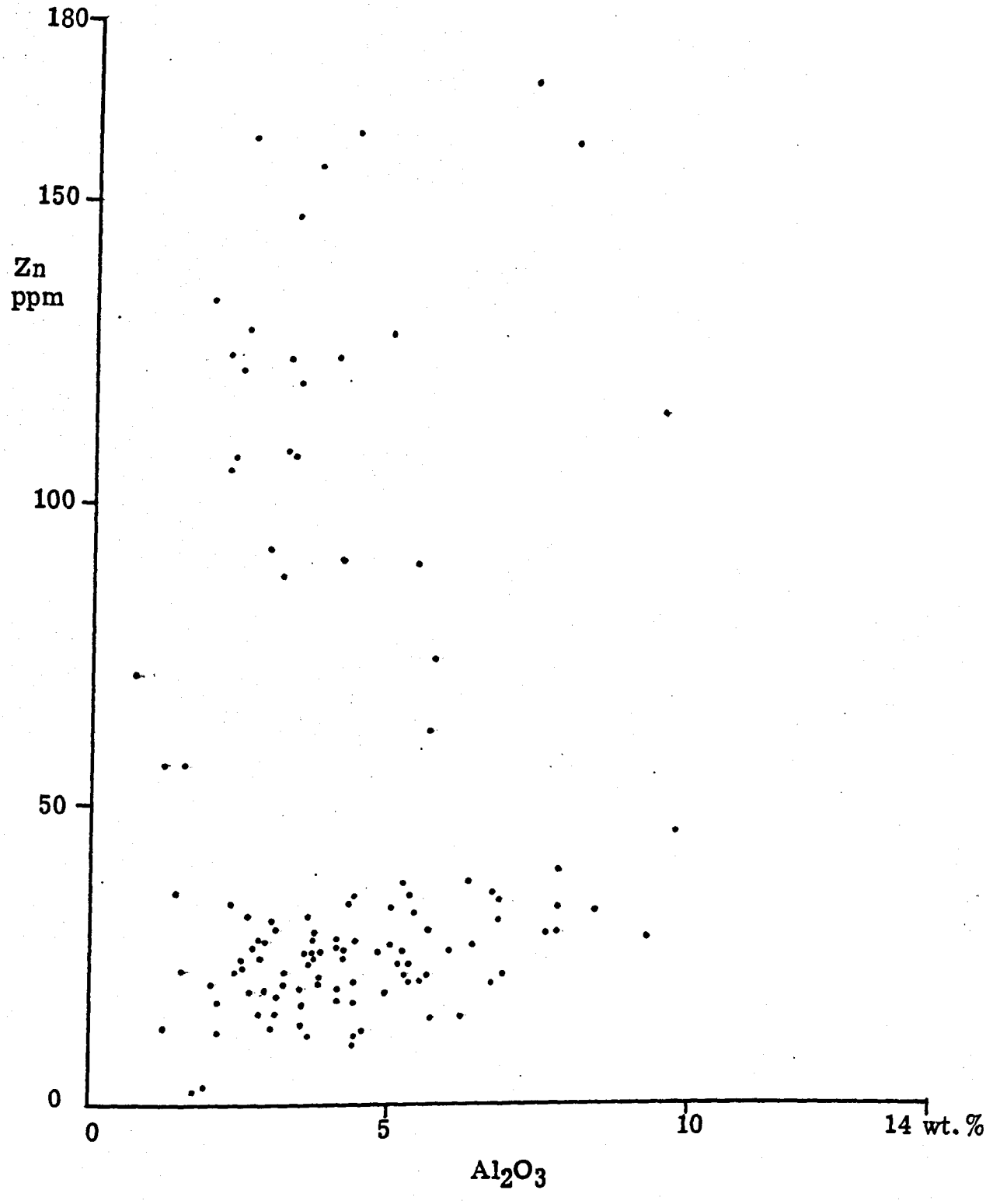


Fig. 6.12 : Plots of Al_2O_3 wt. % against Zn. ppm

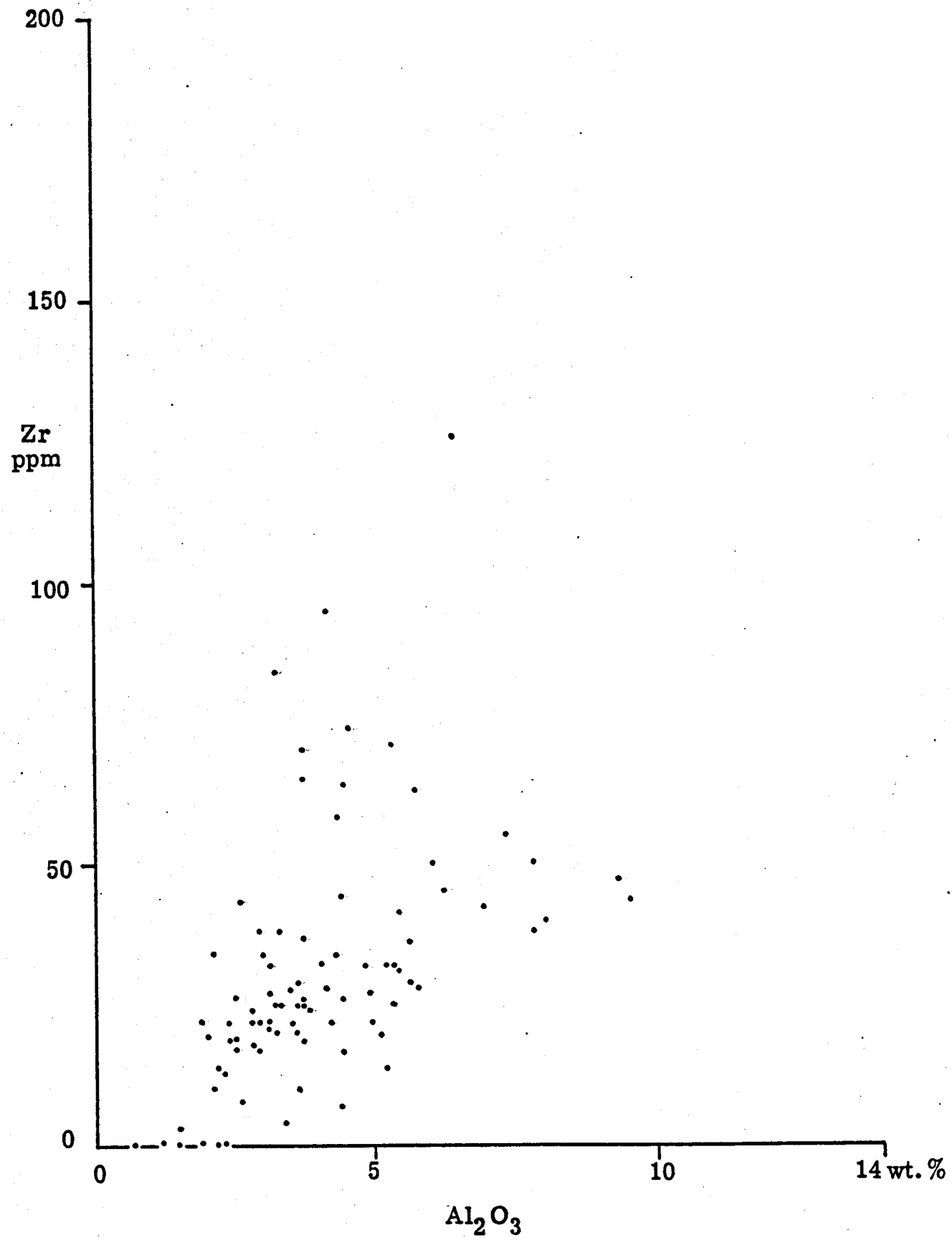


Fig. 6.13 : Plots of Al_2O_3 wt. % against Zr. ppm

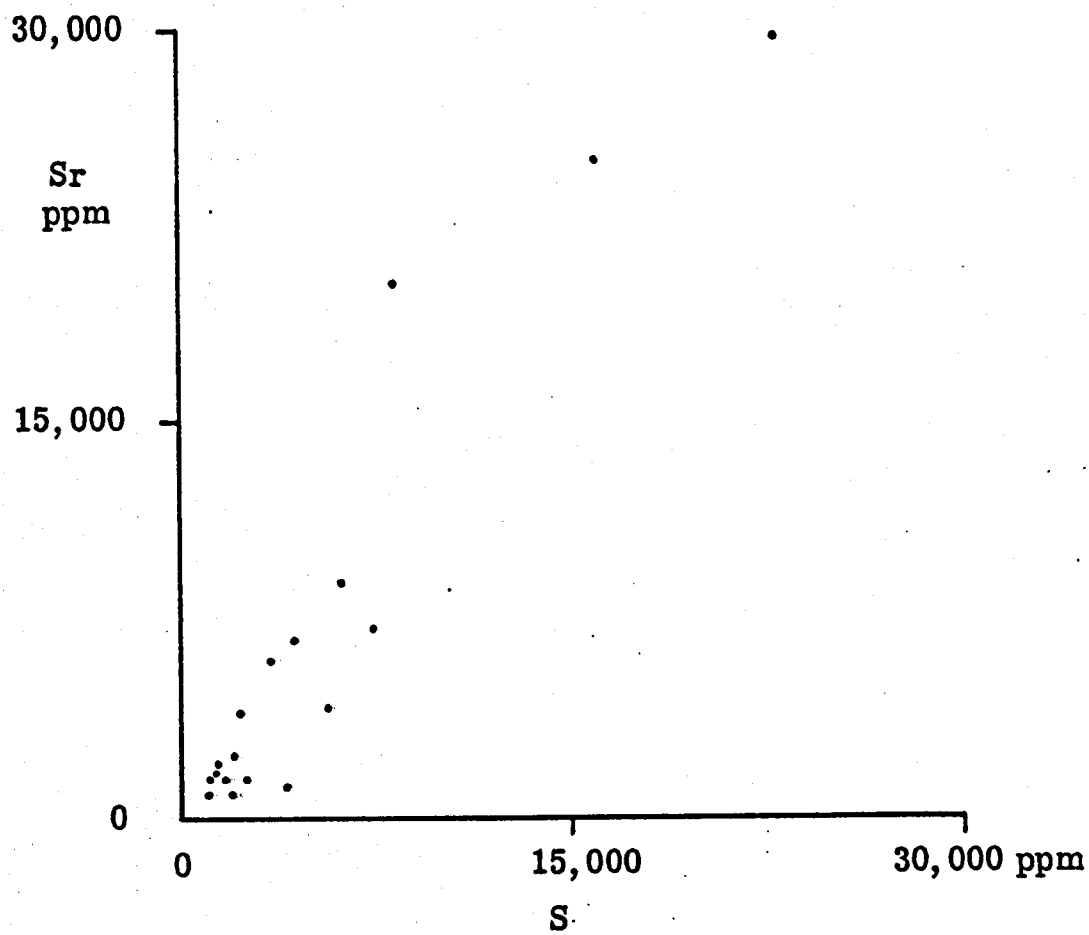


Fig. 6.14 : Plot of S against Sr (ppm)

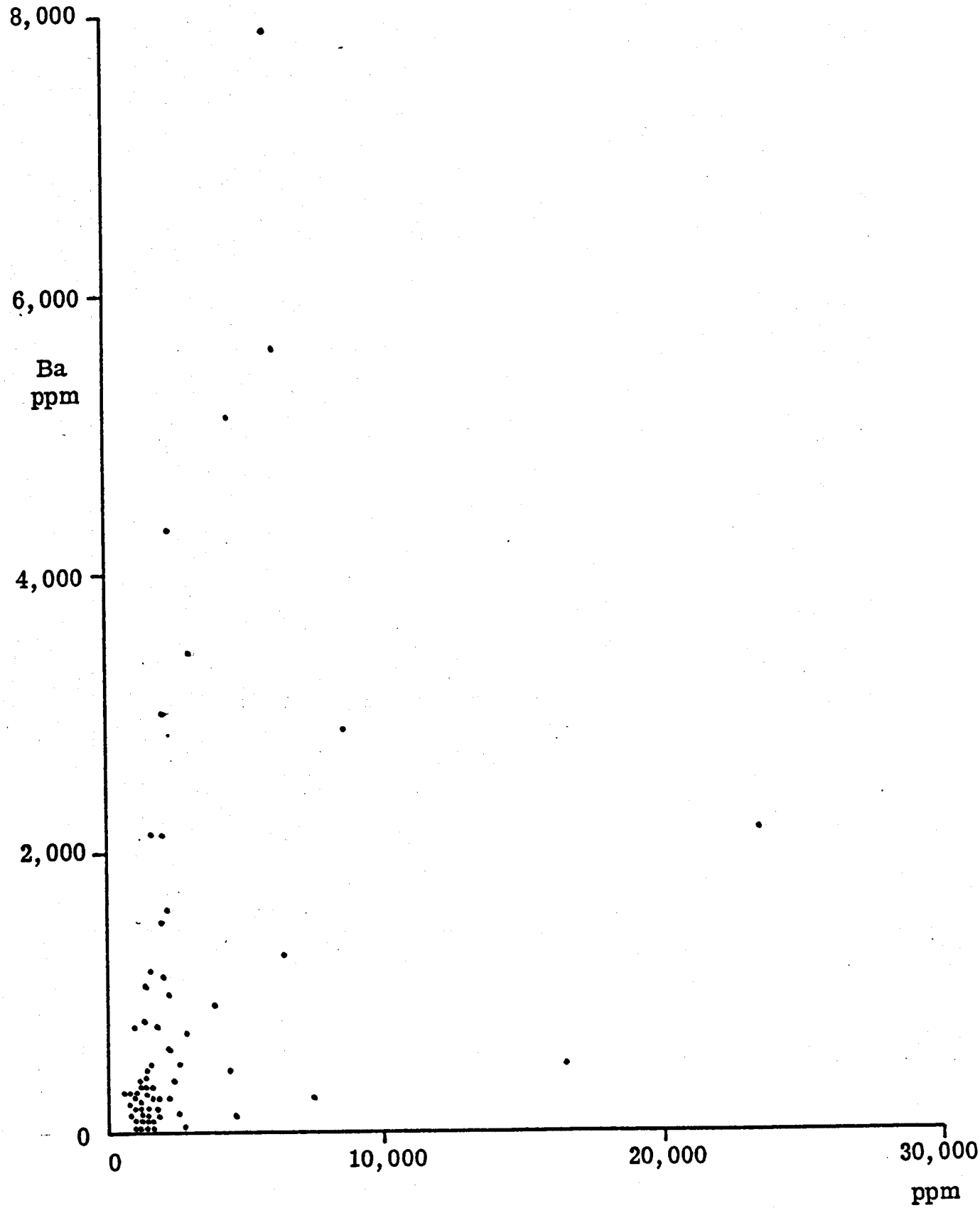


Fig. 6.15 : Plots of S against Ba (ppm)

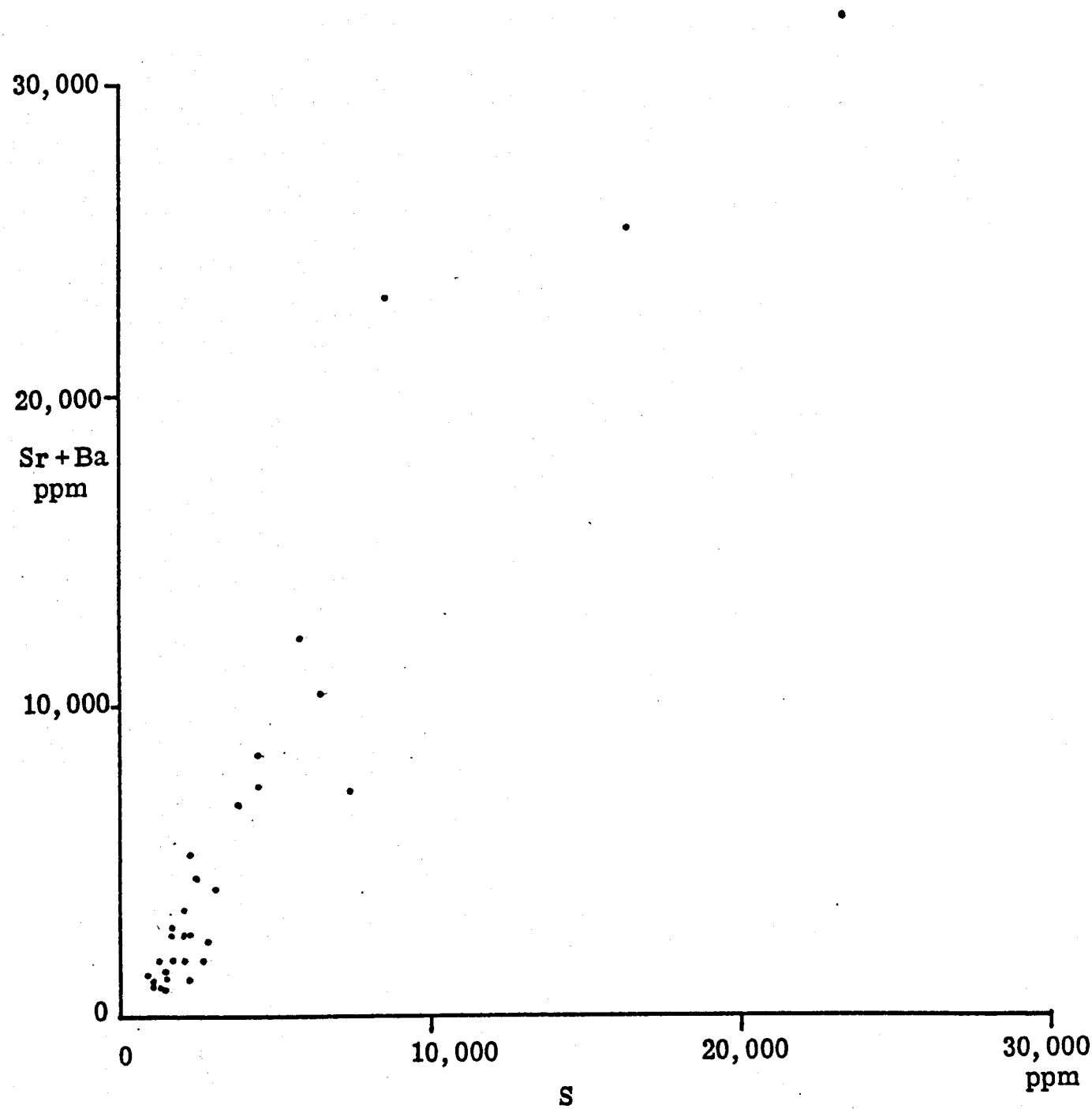


Fig. 6.16 : Plot of S against Sr + Ba (ppm)

6.2 Computation of Mineral Proportions from the Chemical Analyses

The calculation of the modal composition of the rocks from the chemical analyses is especially useful for fine-grained sedimentary rocks where modal analysis of thin sections is extremely difficult, Imbrie and Poldervaart (1959); Nicholls (1962); Miesch (1962) and Pearson (1978) have outlined procedures. Nicholls (1962) has pointed out that the variability of clay mineral compositions make such calculations difficult but if the methods of Imbrie and Poldervaart (1959) and Miesch (1962) are used to identify the probable types of clay minerals a plausible result can be obtained and these methods are used here.

Thus the following chemical compositions of the clay minerals are used :

Illite $2K_2O \cdot 3MgO \ (Al_2O_3, Fe_2O_3)_8 \cdot 24SiO_2 \cdot 12H_2O$

Montmorillonite $(Al_2O_3, Fe_2O_3)_2 \cdot 8SiO_2 \cdot 2H_2O$

Chlorite $4MgO.2Al_2O_3 \cdot 2SiO_2 \cdot 4H_2O$

Some adjustment of the Al_2O_3/Fe_2O_3 ratio and SiO_2 - content was occasionally necessary in order to combine as much of the material into the above minerals as possible. As a result of their relatively minor concentrations, the four oxides (TiO_2, MnO, Na_2O and P_2O_5) were excluded from the computation. Their contents are so small that whether or not they are considered makes no significant difference.

Essentially/

Essentially the procedure assumes the following steps:

1. Convert the wt% of the various oxides into molecular proportions by dividing the oxide wt% by the corresponding molecular weight. Five decimal places, from which decimal points and zeros are eliminated, are carried out in calculation. Each molecular proportion is designated by a capital letter as some require to be referred to again.

2. Calculate the sulphate minerals by multiplying molecular proportions of the key oxides by the appropriate molecular weight.

3. Calculate carbonates as follows :

   From the molecular proportion of CO_2 subtract the proportion of CaO remaining after allowing for CaO used in gypsum. The balance F represents the amount of dolomite necessary to use up all of the CO_2. By subtracting F from the available CaO, the molecular proportion of calcite is determined.

4. The quantities H, J, K, L and M represent the proportions of MgO, K_2O, Fe_2O_3, Al_2O_3 and SiO_2 available for clay, haematite and quartz. All of K_2O is computed as illite, remaining MgO is computed as chlorite, after forming these two clay minerals the remaining Al_2O_3 is computed as montmorillonite. The remainder of Fe_2O_3 and SiO_2 after forming clay minerals is computed/

The calculation form used in this study :

SO_3	÷	80.06	=	A				
SrO	÷	103.62	=	B	× 183.69		=	% Celestine
		A − B	=	C				
BaO	÷	153.34	=	D	× 233.42		=	% Baryte
		C − D	=	E	× 172.18		=	% Gypsum
CO_2	÷	44.01			=			
CaO	÷	56.08	=	−E=	−F=	× 100.09	=	% Calcite
MgO	÷	40.32	=	G −F =	H	F × 184.42	=	% Dolomite
K_2O	÷	94.20	=	J				
Fe_2O_3	÷	159.70	=	K				
Al_2O_3	÷	101.96	=	L				
SiO_2	÷	60.06	=	M				
H_2O *								
Total								

K_2O	J	÷	2	=	N	× 2898.20	=	% Illite
MgO	H	÷	4	=	−.75	= P × 557.40	=	% Chlorite
Al_2O_3	L	− (6N + 2P)	=	÷ 1.5	=	R × 720.42	=	% Montm.
SiO_2	M	− (24N+ 2P +8R)	=			× 60.06	=	% Quartz
Fe_2O_3	K	− (2N + 0.5P)	=			× 159.70	=	% Haematite
H_2O*		2E + 12N + 4P + 2R				× 18.02	=	% H_2O
Total								

Example : Sample MG79

SO_3	1.07 ÷ 80.06	= 1336 A		
SrO	0.14 ÷ 103.62	= 1358 x 183.69		= 0.25% Celestine
		A-B = 1201C		
BaO	0.79 ÷ 153.34	= 515D x 233.42		= 1.20% Baryte
		C-D = 686E x 172.18		= 1.18% Gypsum
CO_2	37.73 ÷ 44.01		= 85731	
CaO	35.60 ÷ 56.08	= 63481 - 686	= 62795-22936= 39859x100.09	= 39.89% Calcite
MgO	9.35 ÷ 40.32	= 23189-22936=253	22936x184.42	= 42.30% Dolomite
K_2O	0.63 ÷ 94.20	= 669 J		
Fe_2O_3	1.09 ÷ 159.70	= 683 K		
Al_2O_3	2.57 ÷ 101.96	= 2521 L		
SiO_2	9.17 ÷ 60.06	= 15268 M		
H_2O *	1.06			
Total	99.20			

K_2O	669 ÷ 2 = 335 x 2898.20	= 9.71% Illite
Al_2O_3	2521 - 2010 = 511 ÷ 2 = 256 x 720.42	= 1.84% Montm.
SiO_2	15268 - (8040+2048) = 5180 x 60.06	= 3.11% Qtz.
H_2O *	1372+4020+512 = 5904 x 18.02	= 1.06% H_2O
Total (excluding H_2O)		= 99.48%

Example: Sample MG 182

SO_3 0.27 ÷ 80.06 = 337A

SrO - = - B

A-B = 337C

BrO - = - D

C-D = 337E x 172.18 = 0.58% Gypsum

CO_2 35.31 ÷ 44.01 = 80232

CaO 28.51 ÷ 56.08 = 50838-337 = 50501-29731=20770x100.09=20.79% Calcite

MgO 14.14 ÷ 40.32 = 35069-29731 = 5338H 29731F x184.42 = 54.83% Dolomite

K_2O 0.51 ÷ 94.20 = 541J

Fe_2O_3 3.22 ÷ 159.70= 2016 K

Al_2O_3 4.24 ÷ 101.96= 4158 L

SiO_2 11.58 ÷ 60.06= 19281M

H_2O * 1.57

Total 99.35

K_2O 541 - 2 = 271N x 2898.20 = 7.85% Illite

MgO 5338H ÷ 4 = 1334-203=1131 x 557.40 = 6.30% Chlorite

Al_2O_3 4158L -(1626+2262) = 270 - 2 = 135x720.42 = 0.97% Montm.

SiO_2 19281M-(6504+2262+1080) = 9435x60.06 = 5.67% Qtz.

Fe_2O_3 2016K-542 = 1474 x 159.70 = 2.35% Haematite

H_2O* 674+3252+4524+270 = 8720 x 18.02 = 1.57% H_2O

Total (excluding H_2O) = 99.34%

computed as haematite and quartz respectively. The amount of H_2O is computed on the basis of hydrous minerals according to their formulae used here.

Imbrie and Poldervaart (1959) found their results compared well with X-ray and insoluble residue data, and they estimated the method to give the clay; dolomite; calcite and chert contents to within 5%. The present results obtained are very satisfactory on the grounds that generally the contents of CO_2; CaO and MgO and K_2O; Fe_2O_3; Al_2O_3 and in some instances MgO, match reasonably stoichiometrically to give carbonates and clay minerals.

The results show that 66% of the samples contain between 50 and 73% dolomite, so that most of the carbonates in the Ballagan Formation are dolomites. Calcite is found to be the second important mineral varying between 9 and 86% and clay is the third ranging between 3 and 39%.

Illite is the predominant clay mineral followed by montmorillonite and chlorite. Many other investigators reported the predominance of illite, amongst them, Keller (1956), Dunbar and Rodgers (1957), Deer et al (1966), and Pettijohn (1975). The presence of illite in every sample and its occurrence as the commonest clay mineral may indicate that at least part of it is authigenic. Thus Deer et al (1966) believe that illite in some occurrences is derived by alteration of other clay minerals during diagenesis/

diagenesis. However, Weaver (1958) concluded that any of the major clay minerals can occur in abundance in any of the major depositional environments and the majority of clay minerals in sedimentary rocks are detrital in origin, they strongly reflect the character of their source material, but suffer only slight modification in their depositional environments. Similar conclusion was drawn by Taggart and Kaiser (1960).

The illite, montmorillomite and chlorite association in some analyses perhaps is resulting from their interstratification on a microcrystalline scale but the environmental significance of such mixed-layer clay is imperfectly understood Keller (1956).

Obviously K is essential to the composition of illite and the abundance of this clay mineral is likely to indicate that the parent rock contained K in appreciable amounts, this rock is, therefore, most likely to be K - feldspathic.

After forming the clay minerals excess SiO_2 is computed into quartz and 52% of the analyses contain between 1 and 20%.

Calculated haematite appears in only two sections, Little Corrie and Ballagan Glen. Either different clay composition or, more likely, the actual presence of haematite must be responsible for this.

The/

The computed sulphate minerals are less common but their presence is of great significance with respect to the interpretation of the depositional environment as they suggest evaporative conditions.

Plots of the computed major minerals on a triangular diagram (Figs. 6.17-23) showing dolomite; calcite and total terrigenous fraction (clay + quartz + haematite), indicate that the majority of analyses tend to fall in the dolomite region, less analyses have the tendency towards calcite, while only those analyses with relatively high quartz content are close to the terrigenous material. These are not considered to be carbonates as they usually contain less than 50% carbonates. There is, therefore, a considerable abundance of terrigenous material. The purpose of plots being made for the individual sections on this diagram is principally to show that the compositions of the rocks under study in the different logged sections are generally similar.

Plots of the total terrigenous material fraction against calcite and dolomite are shown on Figs. 6.24 and 6.25 respectively. Good correlation is evident only in some analyses in the case of calcite, these apparently are either devoid of dolomite or contain minor amounts of it. In the case of dolomite, a significant number of the analyses reveal a fair correlation. The author assumes that the terrigenous material had a role, possibly an important/

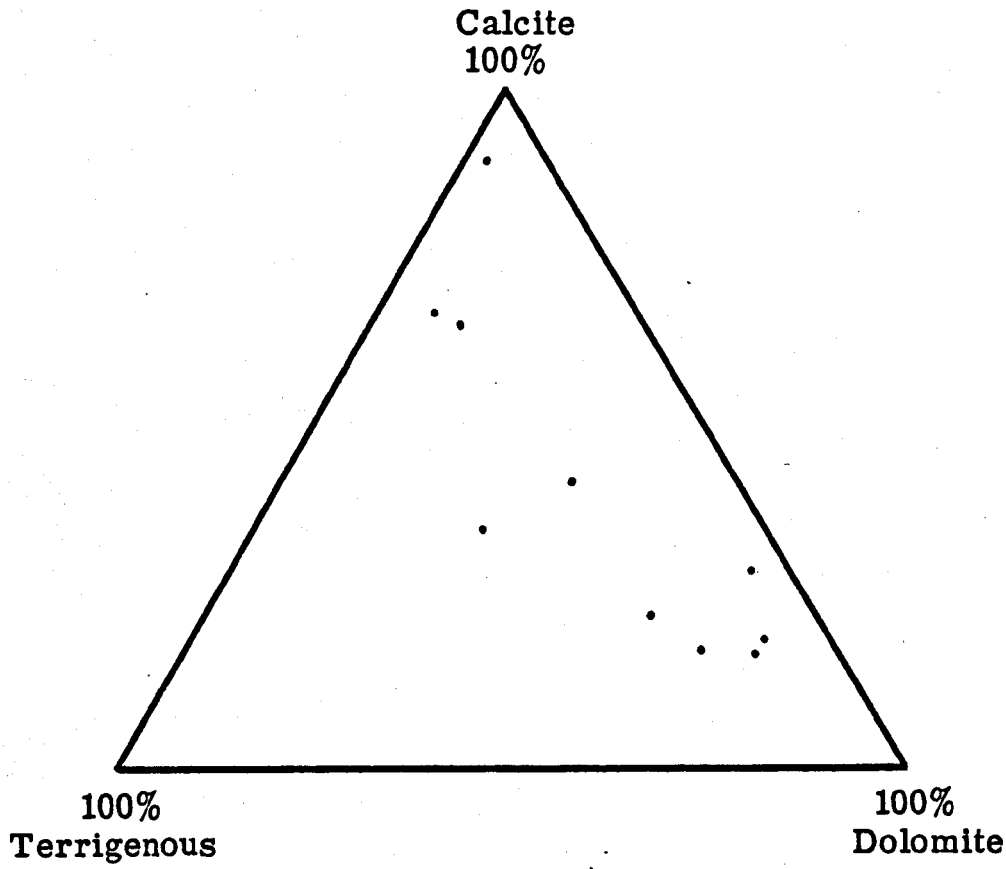


Fig. 6.17 : The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Loch Thom.

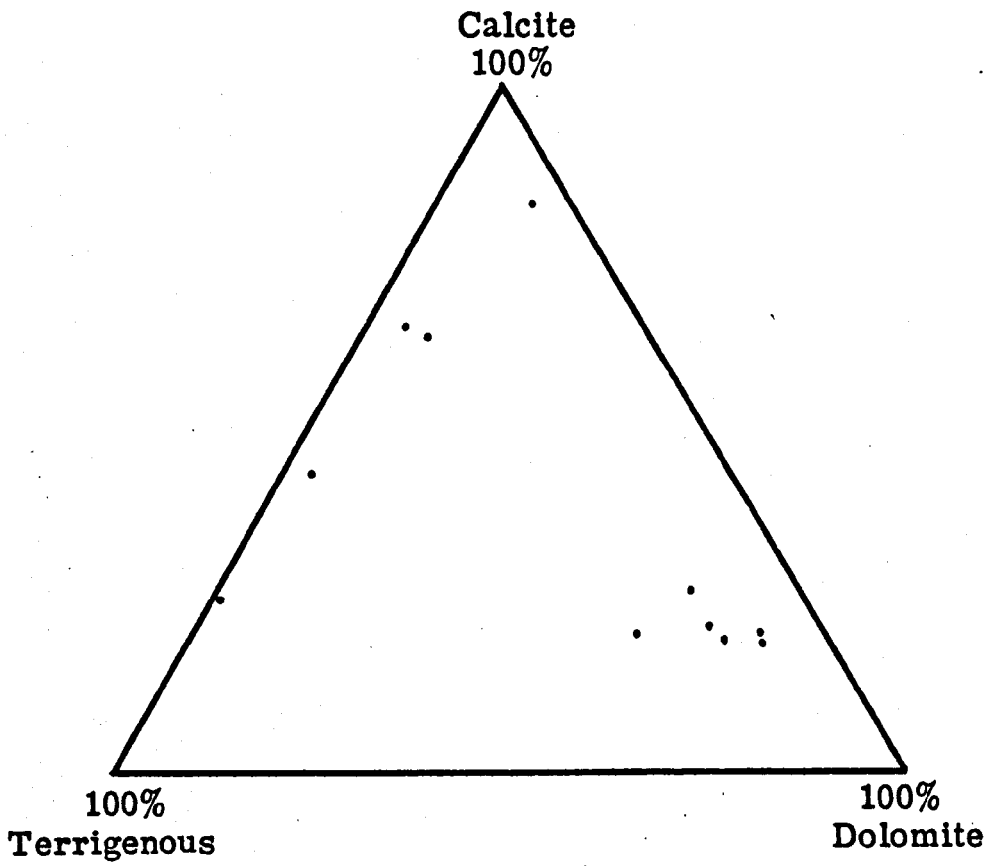


Fig. 6.18 The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Ben Bowie, Helensburgh

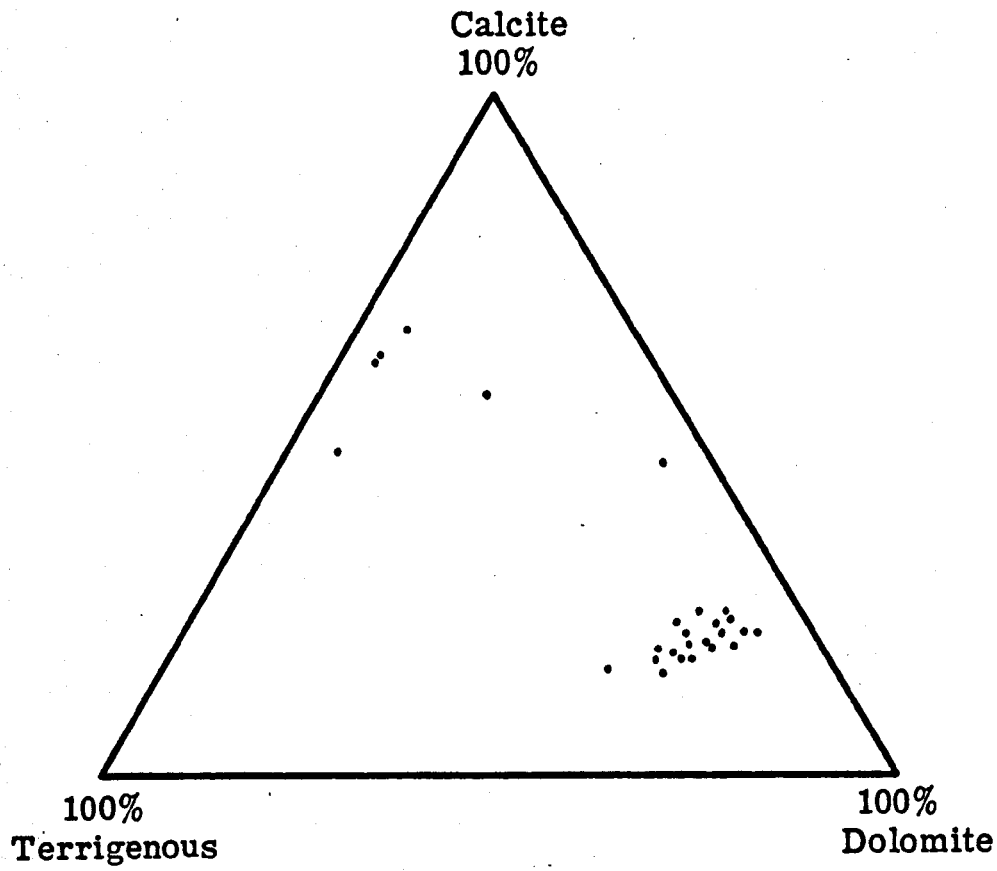


Fig. 6.19 : The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Auchenreoch Glen, Dumbarton.

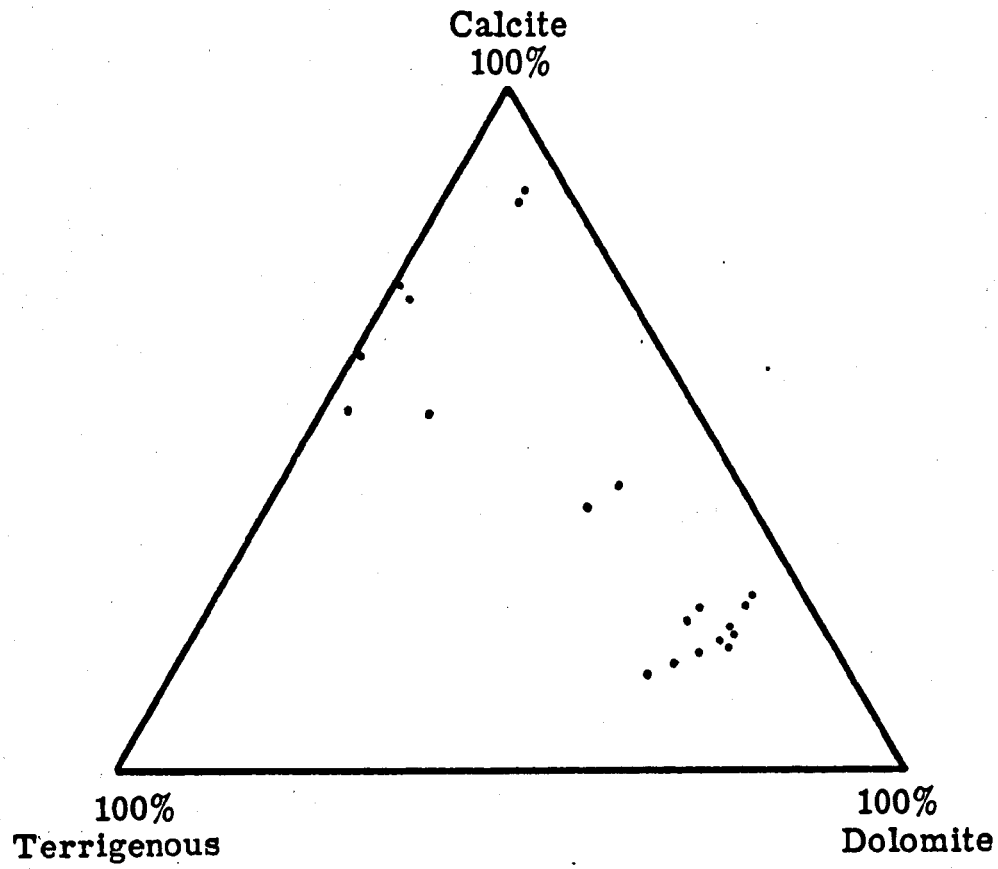


Fig. 6.20 : The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Overtoun Burn, Dumbarton

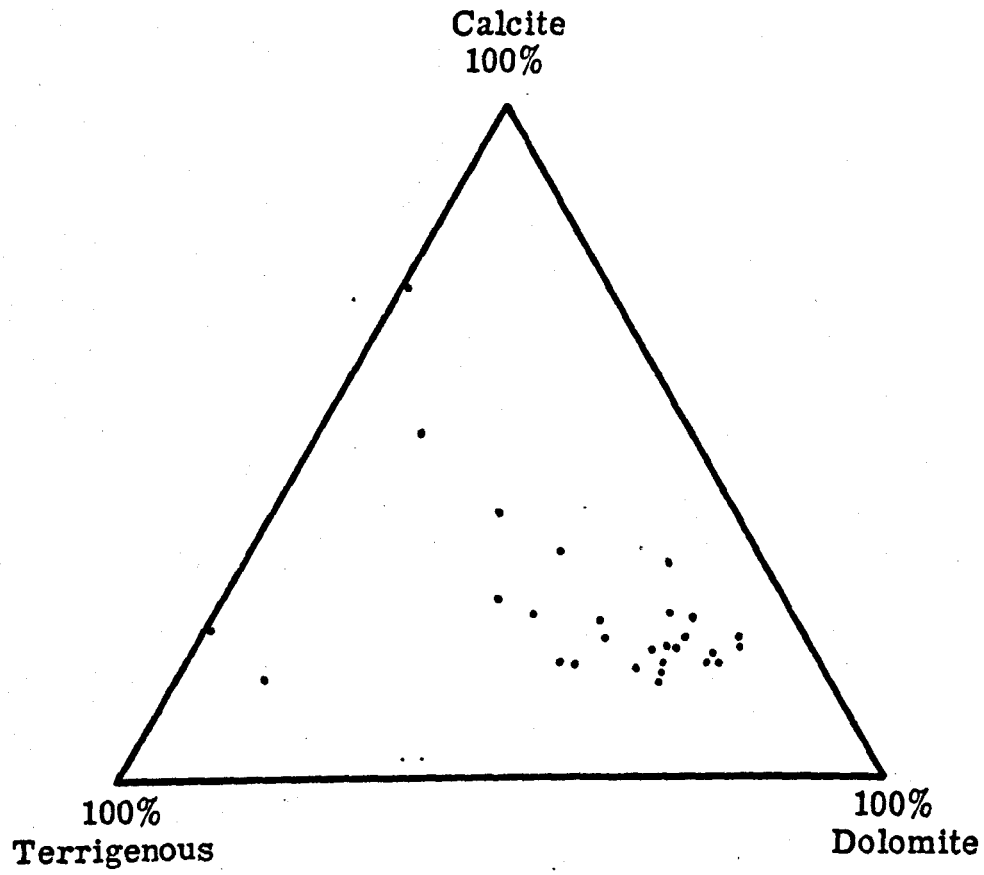


Fig. 6.21 : The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Gargunnock Burn, Gargunnock.

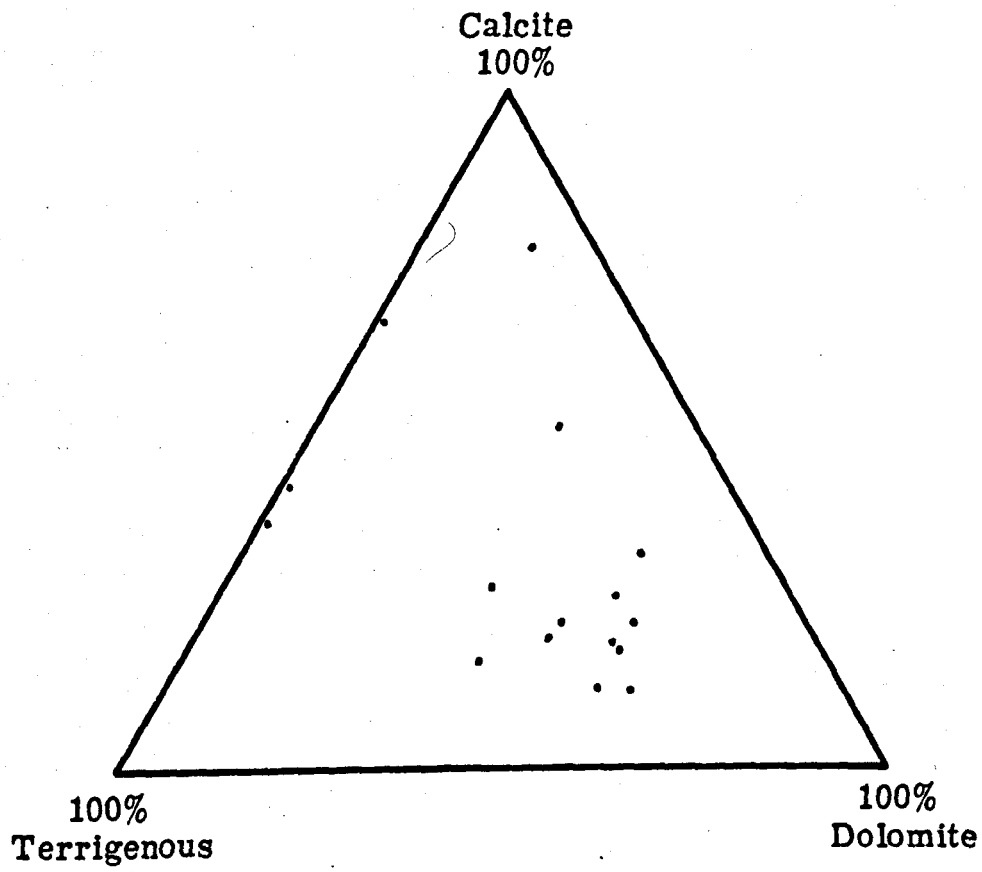


Fig. 6.22 : The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Little Corrie, near Fintry.

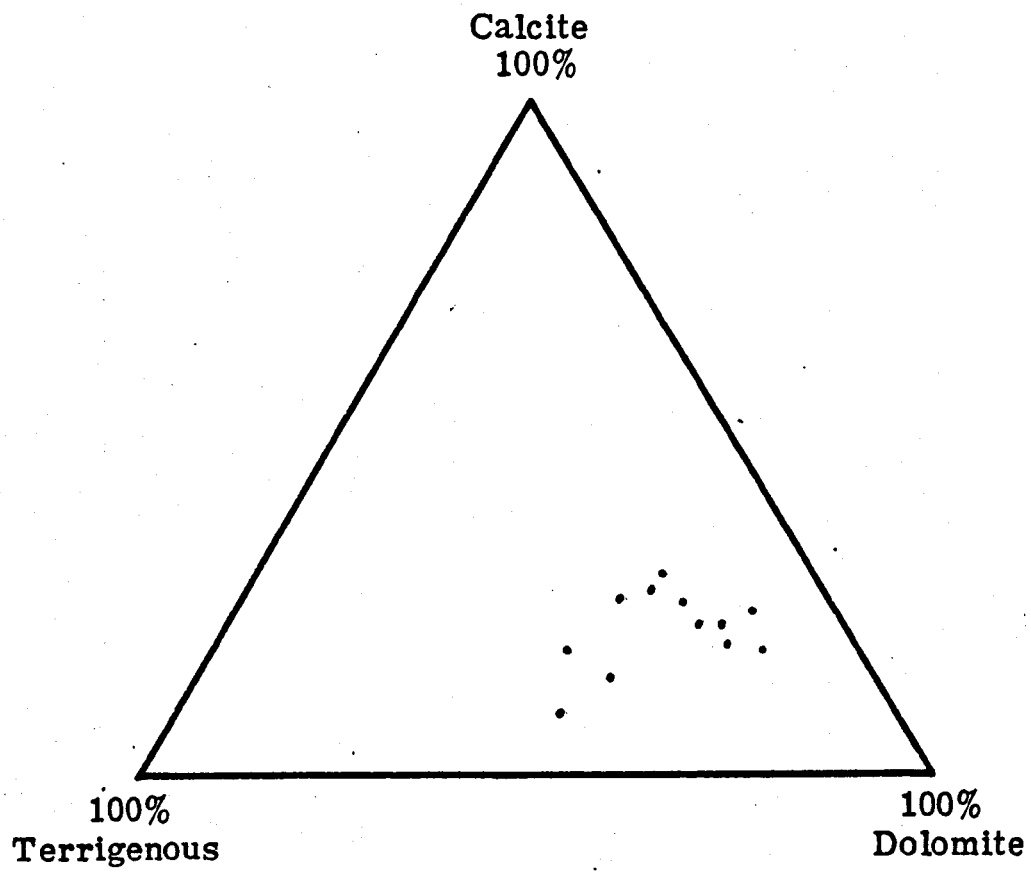


Fig. 6.23 : The compositions of carbonate intervals in the Ballagan Formation as computed from chemical analyses. Ballagan Glen, Strathblane.

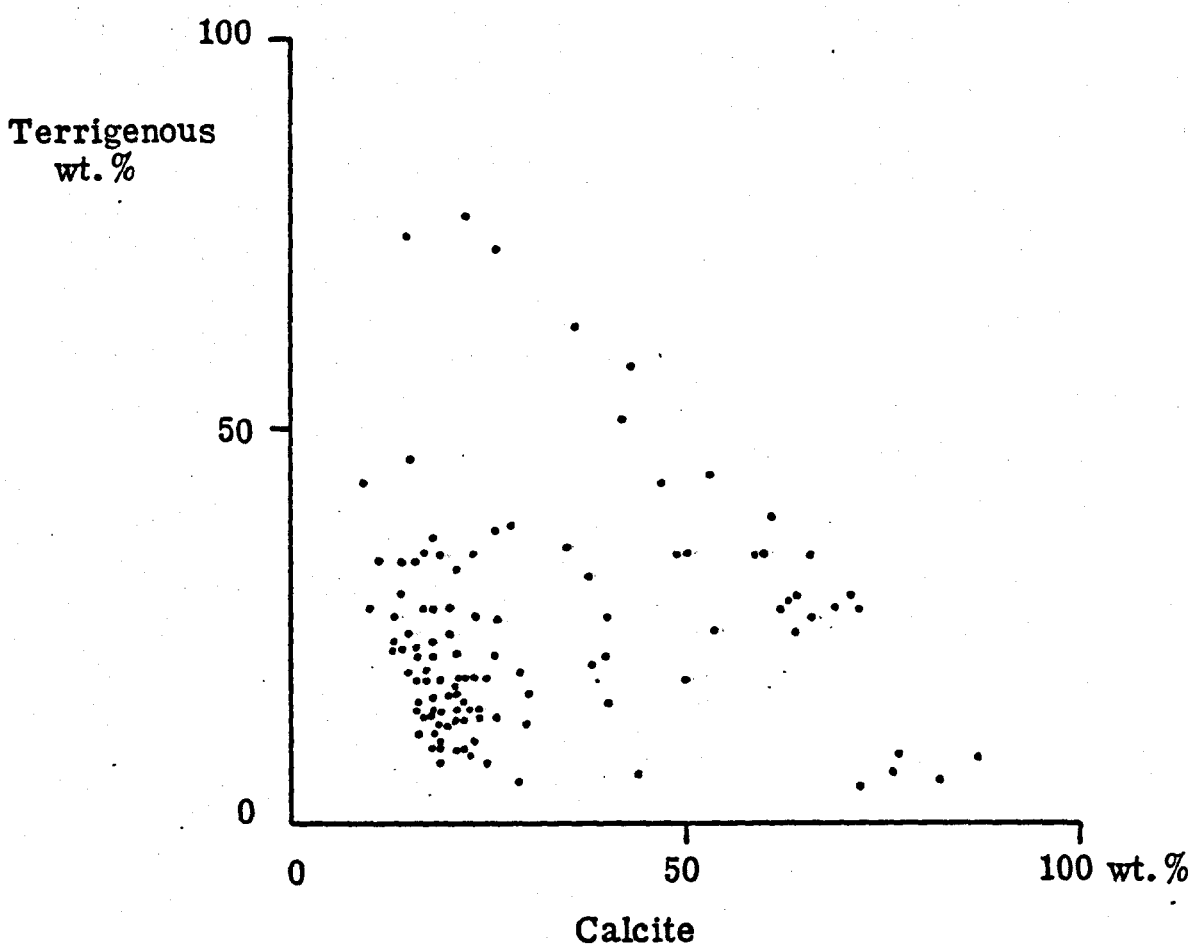


Fig. 6.24 : Plots of Calcite against Terrigenous material computed from chemical analyses.

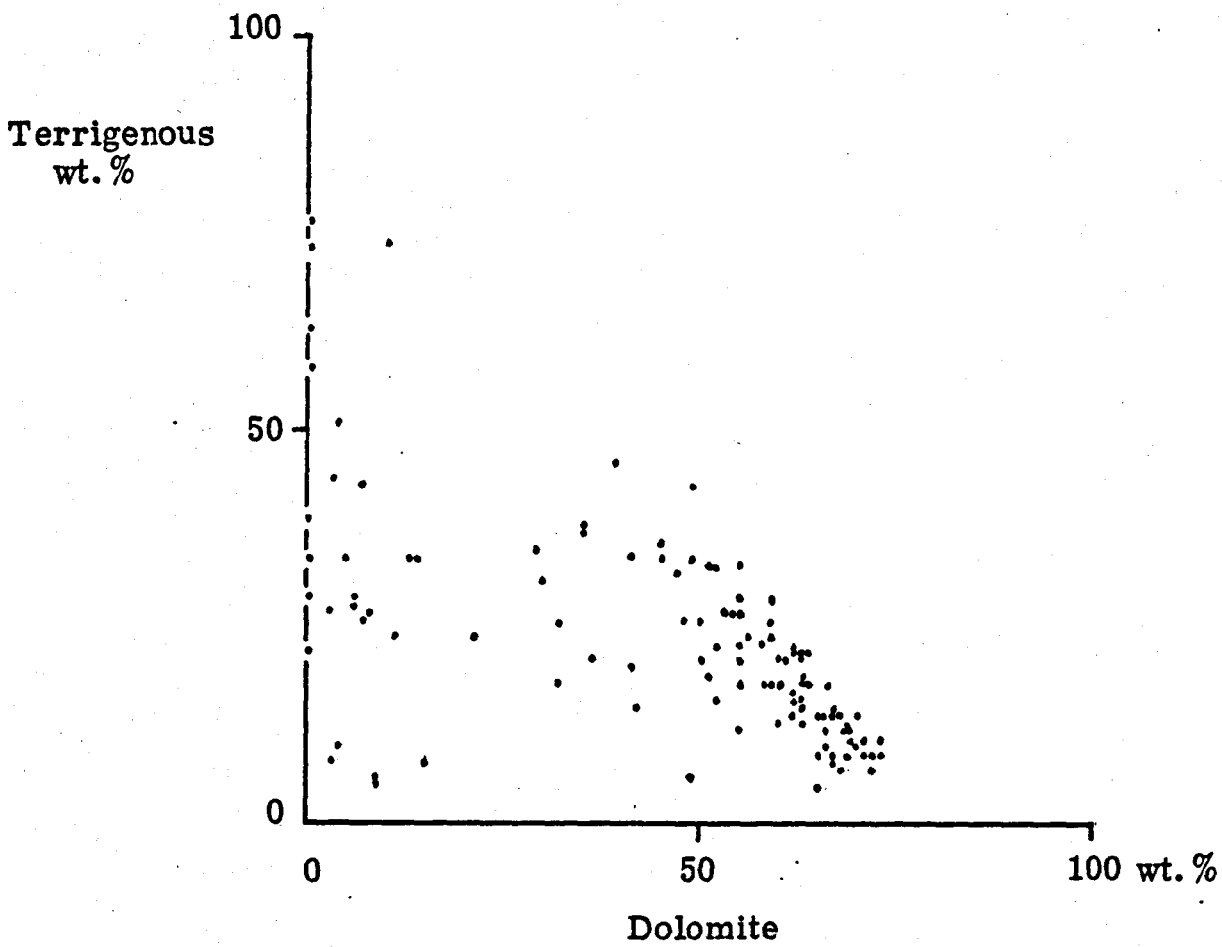


Fig. 6.25 : Plots of Dolomite against Terrigenous material computed from chemical analyses.

important one, to play in the formation of carbonates in general. It is evidently difficult to speculate as to what degree and in which manner it has effected the calcite-dolomite proportion since the analyses show a wide range of calcite-dolomite-terrigenous material associations. Therefore, the controlling factor(s) of the calcite-dolomite proportion will be considered in the section on the depositional environment.

A histogram of Ca/Mg ratios (Fig. 6.26) calculated from the computed carbonate minerals indicates that the majority of analyses are dolomites in terms of Chilingar's (1957) classification, less commonly analyses are distributed between calcitic dolomite and dolomitic limestone. Only a few analyses are found devoid of dolomite, namely, non-dolomitic limestone. A histogram of Ca/Mg ratios (Fig. 6.27) of the total composition give a similar result irrespective of the amount of Mg contained in the clay fraction.

The general conclusion that can be drawn from the plots and histograms is that the rocks involved in the present study are mainly dolomites with minor limestone occurrences.

Plots of the frequency distribution of the calcite - dolomite mixtures occurring in the carbonate rocks of the Ballagan Formation were made after the actual carbonate content was recalculated to 100% assuming the rocks are pure carbonates. This histogram (Fig. 6.28) resembles that of Graf (1960, p.22, Fig. 3a) with the exception/

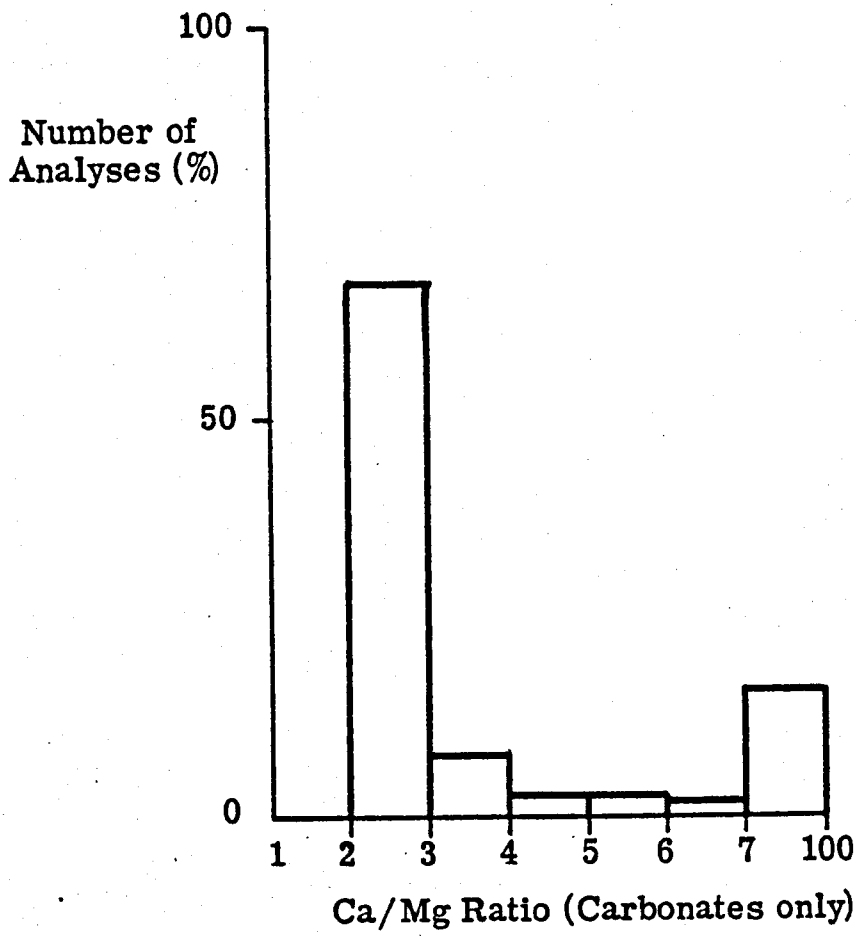


Fig. 6.26 : The frequency distribution of Ca/Mg Ratio for carbonate portion only.

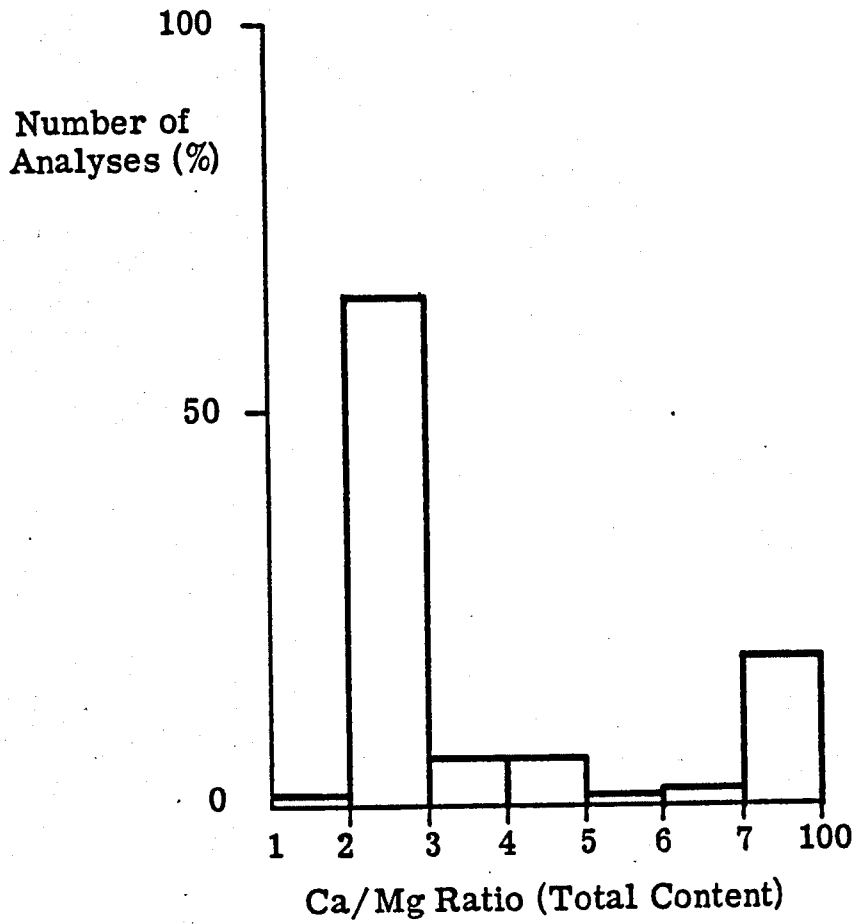


Fig. 6.27 : The frequency distribution of Ca/Mg Ratio for their total content.

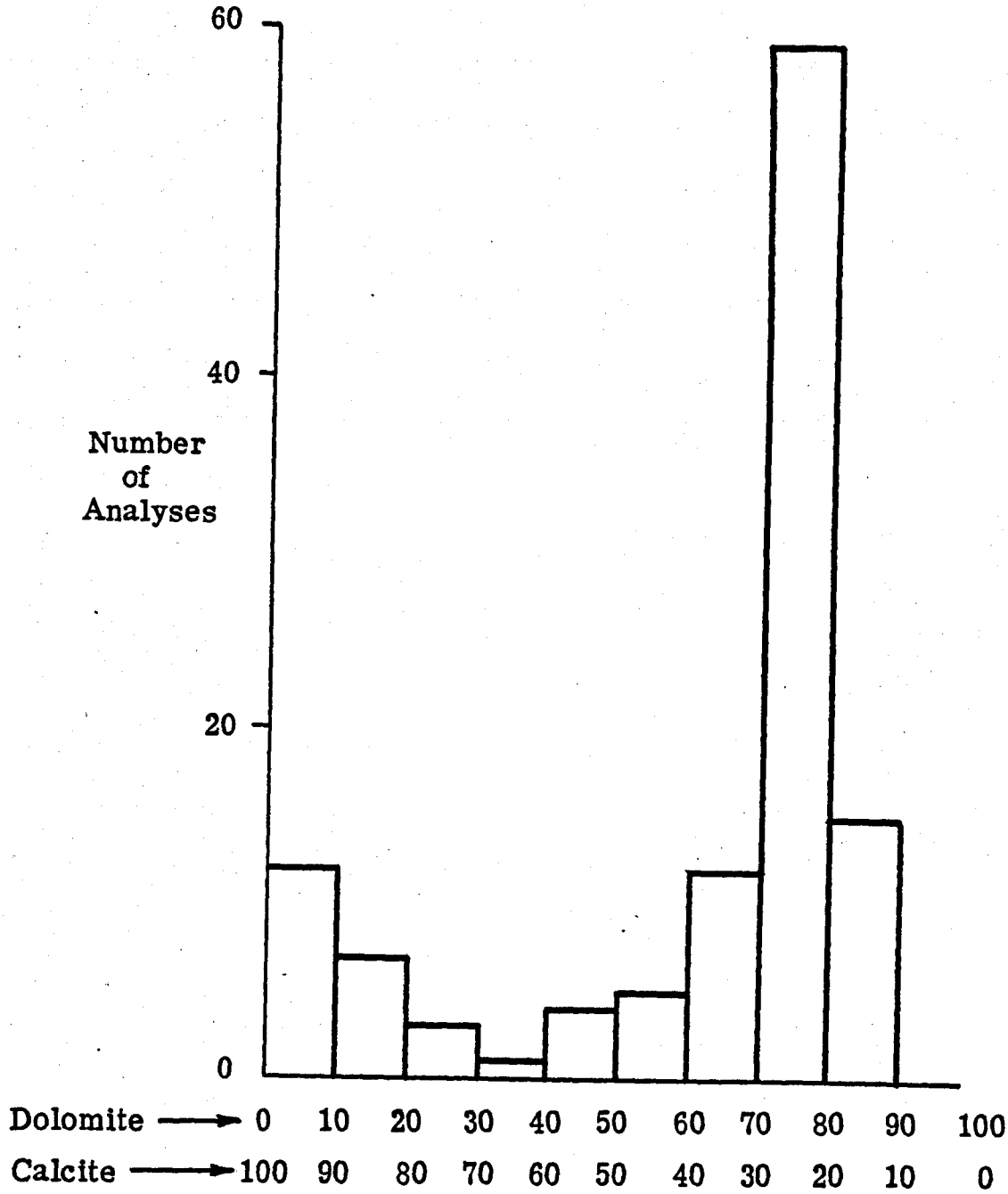


Fig. 6.28 The frequency distribution of Dolomite-Calcite mixtures of rocks containing more than 50% total carbonates. Dolomite and Calcite made up to 100%

exception that dolomite does not exceed 90% in the present study. The occurrence of two maxima near both ends of the range is interpreted by Graf (1960) as a likely result of the two ends of the range being reinforced statistically by carbonate rocks of special types, in the one case by fine-grained, virtually pure, supposedly chemically precipitated dolomite rocks from evaporite sequences, in the other by the weakly dolomitized rocks in which very local redistribution of the Mg originally in biogenic magnesian calcites is adequate to account for the dolomite present.

Although the rocks of the present study do not contain as much dolomite as those of Graf (1960), the occurrence of the maximum near the end of the range on the side of 100% dolomite is ascribed to the same reason on the grounds that a primary chemical precipitation in an evaporative environment is suggested to be the most likely origin of these dolomites as indicated by the homogeneity and fineness of the minerals; the absence of fossils; the occurrence of evaporite minerals such as gypsum; and the general agreement by numerous workers of this origin for analogous rocks. With regard to the calcite end, it is believed that the maximum occurrence is caused by either the original absence of dolomite or the segregation of calcite as supported by the presence of calcite clots.

6.3/

6.3 Conclusions

The bulk rock geochemistry of the carbonate layers in the Ballagan Formation is generally indicative of the domination of the original sediment by carbonate minerals, predominantly dolomite with calcite as the second in abundance. These carbonates are found to demonstrate various associations with clay minerals, mainly illite, and less common, detrital quartz and feldspar. Haematite presence is indicated by the high Fe_2O_3 concentrations in the analyses from Little Corrie, near Fintry (Grid Ref. 578 850) and Ballagan Glen, near Strathblane (Grid Ref. 572 795) sections. The carbonate layers are usually enclosed in lutite beds the thickness of which is of a very wide range, occasionally they are found in contact with sandstones.

The petrographical and stratigraphical characteristics of the carbonates indicate that they have formed as primary chemical precipitates, in an environment of deposition, which may be to some extent similar to the present situation in the Coorong region, South Australia.

The chemistry of the original sediments has certainly been modified, in part at least, as evidenced by the development of neomorphic and metasomatic microfabrics. These phenomena have been tested by electron microprobe analysis (Tables 6.14, 6.17, 6.18 and 6.22).

The/

The contents of trace elements with the exception of S, Sr and Ba are assumed to be derived from the clay fraction as inferred from the good correlation between some of them and Al_2O_3.

Renov and Ermishkina (1959 in Leake et al, 1975) claim that low Fe/Mn ratios in carbonates are indicative of near-shore environments, if true this will be additional evidence in support of the assumption that these carbonates were formed in a lagoonal environment as their Fe/Mn ratios range from about 1.00 - 9.00 but generally below 5.00.

According to Veizer and Demovic (1974) the range of Sr concentrations in the late diagenetic dolomites is 30-100 ppm, and the measured values of Sr concentrations in early diagenetic dolomite (penecontemporaneous) are between 100-600 ppm. These measurements will obviously assign the dolomites of the present study to the category of early diagenetic origin as their Sr concentrations generally lie within the cited range.

The role of the terrigenous material fraction in the determination of the formed amounts of carbonates is obvious, but whether or not it played any significant role in the determination of the calcite-dolomite proportion and in what manner, is not evident from the geochemistry as a result of the analyses showing a rather wide range of associations in terms of calcite-dolomite-terrigenous material proportions, also no element of those analysed showed any diagnostic/

diagnostic property. However, speculation on this aspect is not attempted.

According to the above mentioned observations with respect to the origin of dolomites Weber's (1964) hypothesis may be applicable and that is they represent very slowly forming truly primary precipitates of very fine grain size, co-precipitated with possibly authigenic clay minerals (mostly detrital in the present investigation) but not appreciable aragonitic or organic component, in a basin of above normal salinity.

6.4 Electron Microprobe Analysis

Electron microprobe analyses were carried out using the EDS system. These analyses were directed at the three microfacies identified in the petrographic study in addition to veinlets and cavity-cement. Many of the rocks under investigation are so fine-grained that probe analysis of the individual minerals is extremely difficult. The probe analyses are, therefore, neither the compositions of individual minerals nor that of the bulk composition of the rock but are used solely to indicate the range of minerals present, in a qualitative not a quantitative manner.

Analyses of Microfacies A (Tables 6.9 and 6.10) and Microfacies B (Tables 6.11 and 6.13-15) show that the crystals of the latter contain comparatively less impurity. This difference in impurity/

impurity-content in the crystals is attributed to the fact that Microfacies B is believed likely to be produced from Microfacies A through neomorphism. This neomorphic process resulted in the rejection of the impurity by the newly formed crystals possibly partially as evidenced by its presence in minor amounts.

Analyses of Microfacies C (Tables 6.18, 6.19 and 6.23) indicate that it is composed almost exclusively of calcite, associated in some instances with gypsum, celestine and baryte according to the analyses. In some analyses more than one of these sulphate minerals are possibly present (Table 6.22) which may signify their co-existence.

Analyses of the original sediment (Table 6.17) and the coarse calcite clots (Table 6.18) show that the first contains calcite whereas the second is almost clay-free and, therefore, the formation of these clots is considered as a result of segregation of the calcite disseminated in the clay material. Plots of Al_2O_3 against CaO (Figure 6.29) clearly demonstrates the negative correlation between these two oxides which represent clay and calcite respectively, this indicates that the original sediment was constituted of a mixture of these minerals. Plots of Al_2O_3 against MgO gives an excellent positive correlation which may signify the absence of the mineral dolomite (Figure 6.29).

Analyses/

Analyses across a neomorphic dolomite crystal (Table 6.16) and calcite crystals of Microfacies C (Tables 6.20 and 6.21) show that no significant zoning exists. Also, the lack of zoning implies that there were no changes in pore water chemistry during crystal growth. In the case of neomorphism, this may hint at the compositional homogeneity of the transformed material and probably the slowness and continuity of the neomorphic process in order to enable the forming crystals to reject almost all impurity(clay)as if the process were rapid, entrapment of impurity is likely to occur.

The occurrence of celestine is inferred from the presence of sulphur (Table 6.22) in the absence of both calcium and barium which are expected to be alternative elements combing with sulphur in the form of gypsum and baryte respectively. Barium has not actually been analysed by the electron microprobe, but the peak of this element coincides with that of titanium which is not expected to occur in significant amounts. Therefore, in analyses that appear to show large concentrations of titanium (Table 6.24), this is considered indicative of a substantial barium content and, therefore, of baryte. It is obviously difficult, if not impossible, to determine the source of sulphur in the analyses where calcite is present in considerable amounts. It is even more difficult when barium is also present. However, either celestine or gypsum or baryte or a combination of these minerals may be a possible source for the sulphur in a given analysis. The sulphate minerals, as mentioned above, are associated with Microfacies C.

Clay/

Clay is concentrated mainly at the intercrystalline boundaries especially in Microfacies B (Table 6.12) which may substantiate the assumption made earlier with respect to its neomorphic origin from Microfacies A, the concentration is believed to have occurred by the accumulation of the rejected impurity in these sites. In Microfacies C clay is found concentrated in an irregular patches (Table 6.25) presumably as a result of almost total rejection of impurity by the newly formed crystals and their advanced process of development.

The investigation of veinlets indicates that at least three different types are present, namely, ferroan-dolomite (Table 6.26); calcite (Table 6.27); and composite (Table 6.28) veinlets. In the case of the single-mineral veinlets, the minerals concerned are believed to have crystallized from solutions rich in their respective elements. In the composite veinlet, dolomite is found near the wall, then calcite and finally celestine in the centre (Plate 4.5). The controlling factor(s) of such crystallization order of these minerals in a single veinlet, assuming that they are all formed as primary chemical precipitates, is unknown. However, it is assumed that the solution from which they crystallized was rich in the elements Mg; Ca; Sr and SO_4. There is a possibility that the rock being dolomite might have acted as a nucleus for the dolomite portion to form first, followed by calcite as this solution became depleted in magnesium and finally celestine after the remaining calcium was used/

used to form calcite. There is also the possibility that some or even all of these minerals are secondary in origin.

Analyses of a cavity-cement show that it is composed mainly of calcite (Table 6.29). This may indicate that the cavity was occupied by a solution from which only calcite crystallized in amounts sufficient to seal off the cavity.

Table 6.9 Electron Microprobe Analyses. Microfacies A, 0842A

	1	2	3	4	5
SiO_2	9.10	8.20	2.06	2.00	8.15
Al_2O_3	3.03	3.74	0.81	0.96	3.96
TiO_2	-	-	-	0.15	-
Fe_2O_3	-	-	-	-	-
FeO	1.31	1.36	0.54	0.50	1.20
MgO	15.98	16.79	18.27	18.79	17.25
CaO	25.84	24.43	29.17	30.42	26.96
Na_2O	0.43	-	-	-	-
K_2O	1.68	0.75	0.17	0.25	0.71
MnO	0.27	0.17	0.27	0.29	0.18
P_2O_5	-	-	0.42	0.26	0.30
SO_3	0.34	0.47		0.43	0.36
	57.98	55.91	51.96	54.05	59.07

Table 6.10: Electron Microprobe Analyses, Microfacies A, 089

	1	2	3	4
SiO_2	1.09	3.31	3.66	1.87
Al_2O_3	0.60	1.75	2.17	1.19
TiO_2	-	-	0.17	-
Fe_2O_3	-	-	-	-
FeO	1.28	1.37	0.43	0.22
MgO	17.71	18.21	19.84	20.29
CaO	33.95	32.36	30.57	32.67
Na_2O	-	0.85	0.84	-
K_2O	0.15	0.14	0.55	0.15
MnO	0.56	0.57	0.39	0.33
P_2O_5	-	-	-	-
SO_3	-	0.24	0.31	0.41
	55.34	58.80	58.93	57.13

Table 6.11: Electron Microprobe Analyses. Microfacies 8, 0816

	1	2	3	4	5
SiO_2	0.27	0.43	0.52	0.79	0.21
Al_2O_3	0.16	0.43	0.31	0.33	0.29
TiO_2	-	-	-	-	-
Fe_2O_3	-	-	-	-	-
FeO	-	0.50	0.28	0.30	-
MgO	19.33	20.30	20.65	20.37	19.65
CaO	30.42	29.49	28.92	29.08	30.92
Na_2O	-	-	0.35	-	-
K_2O	-	0.14	0.13	0.14	-
MnO	0.17	-	0.27	0.24	0.14
P_2O_5	-	0.20	-	0.19	-
SO_3	0.19	-	-	-	0.29
	50.54	51.49	51.43	51.44	51.50

	6	7	8	9	10
SiO_2	0.38	0.40	-	0.32	-
Al_2O_3	0.16	-	-	-	-
TiO_2	-	-	-	-	-
Fe_2O_3	-	-	-	-	-
FeO	0.25	0.21	0.23	0.21	0.28
MgO	20.03	19.97	19.67	19.97	19.00
CaO	29.32	29.81	30.32	30.29	30.90
Na_2O	-	-	-	-	-
K_2O	-	-	-	-	-
MnO	0.27	0.18	-	0.13	0.28
P_2O_5	-	-	-	0.18	-
SO_3	-	-	0.27	-	0.21
	50.41	50.57	50.49	51.10	50.67

Table 6.12: Electron Microprobe Analyses. Intercrystalline Boundaries, Microfacies 8, 0816

	1	2	3	4	5	6	7
SiO_2	2.19	31.42	24.86	2.68	13.27	10.32	5.72
Al_2O_3	1.04	6.53	9.98	1.21	5.45	4.06	2.71
TiO_2	-	0.34	0.20	-	0.21	0.15	-
Fe_2O_3	-	-	-	-	-	-	-
FeO	0.69	2.36	3.58	0.68	2.31	1.71	1.03
MgO	19.45	10.63	11.70	18.26	15.20	16.01	17.71
CaO	29.03	16.16	14.78	28.28	21.03	23.76	26.77
Na_2O	-	-	-	-	-	-	-
K_2O	0.28	2.11	3.25	0.29	1.67	1.37	0.58
MnO	0.26	0.16	-	-	0.42	0.19	0.14
P_2O_5	-	-	-	-	-	-	-
SO_3	-	-	-	0.16	-	-	-
	52.70	69.71	68.35	52.06	59.56	57.57	54.66

Table 6.13: Electron Microprobe Analyses. Microfacies 8, 0820

	1	2	3	4	5	6
SiO_2	0.36	0.42	0.97	1.81	0.40	0.56
Al_2O_3	0.23	0.28	0.37	0.91	0.25	0.38
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	0.17	0.17	0.88	0.20	0.38	0.90
MgO	20.24	19.40	19.38	19.03	19.37	19.09
CaO	33.04	32.15	32.15	30.93	31.53	31.48
Na_2O	-	-	-	-	-	-
K_2O	-	0.12	0.08	0.27	0.09	-
MnO	0.32	0.37	0.62	0.29	0.30	0.59
P_2O_5	-	-	-	0.20	-	-
SO_3	-	0.26	0.15	0.16	-	-
	54.36	53.17	54.59	53.80	52.32	53.00

Table 6.14 Electron Microprobe Analyses, Microfacies B, 0829 A

	1	2	3	4	5	6	7
SiO_2	1.36	1.12	2.40	2.37	1.55	0.86	1.09
Al_2O_3	0.59	0.51	1.11	0.82	0.69	0.52	0.49
TiO_2	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-
FeO	0.66	0.47	0.81	0.31	0.46	0.37	0.59
MgO	19.50	19.60	19.22	18.58	19.86	20.06	20.24
CaO	29.77	29.88	29.05	29.67	29.72	31.85	30.28
Na_2O	-	-	-	-	-	0.43	-
K_2O	0.11	0.11	0.26	0.27	0.13	0.13	0.16
MnO	0.20	0.25	-	0.23	0.21	0.28	0.22
P_2O_5	0.29	-	0.30	-	-	-	-
SO_3	-	0.21	0.31	-	-	0.32	0.25
	52.48	51.94	53.47	52.24	52.62	54.39	53.32

Table 6.15: Electron Microprobe Analyses. Microfacies 8, 089

	1	2	3	4	5	6
SiO_2	0.45	0.21	0.26	-	0.33	0.38
Al_2O_3	0.34	-	0.81	0.26	0.48	0.59
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	-	-	0.42	-	-	-
MgO	18.99	19.72	21.09	21.05	20.26	19.63
CaO	35.98	33.69	34.52	33.95	34.78	34.77
Na_2O	0.91	-	1.39	0.86	-	-
K_2O	-	-	-	-	-	-
MnO	0.41	0.50	0.41	0.39	0.29	0.32
P_2O_5	0.52	-	-	0.59	0.69	-
SO_3	0.64	0.63	0.37	0.44	0.51	0.41
	58.24	54.75	59.27	57.54	57.34	56.10

Table 6.16 Electron Microprobe Analyses. Cross-Analysis of a Neomorphic Dolomite Crystal, 089

	1	2	3	4	5
SiO_2	0.23	0.17	0.24	-	-
Al_2O_3	0.49	0.61	0.35	0.59	-
TiO_2	-	-	-	-	-
Fe_2O_3	-	-	-	-	-
FeO	-	-	0.23	0.20	-
MgO	22.30	20.74	21.68	20.41	21.35
CaO	31.64	32.34	31.76	33.27	31.17
Na_2O	1.31	0.80	0.77	-	-
K_2O	-	-	-	-	-
MnO	0.30	0.28	-	0.21	0.19
P_2O_5	-	-	-	0.46	-
SO_3	-	-	-	0.35	-
	56.27	54.94	55.03	55.49	52.71

Crystal Analysed

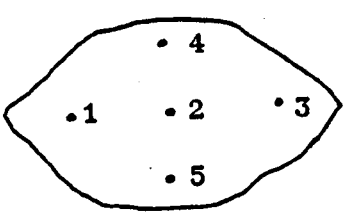


Table 6.17: Electron Microprobe Analyses. Original Sediment, 0839

	1	2	3	4	5
SiO_2	41.07	36.56	37.81	36.28	32.73
Al_2O_3	4.52	14.51	15.88	13.79	13.63
TiO_2	1.00	0.44	0.41	0.52	0.39
Fe_2O_3	-	-	-	-	-
FeO	1.55	6.00	6.24	5.14	5.13
MgO	2.14	6.44	7.52	6.34	6.58
CaO	24.35	9.57	6.14	12.15	10.35
Na_2O	-	-	-	0.36	-
K_2O	1.35	4.56	4.48	4.28	4.12
MnO	0.25	-	-	-	-
P_2O_5	-	-	-	-	-
SO_3	-	0.21	0.19	-	0.20
	76.23	78.29	78.67	78.86	73.13

	6	7	8	9	10
SiO_2	31.39	28.50	34.48	29.13	36.55
Al_2O_3	13.30	11.82	14.86	11.91	16.40
TiO_2	0.43	0.39	0.40	0.31	0.26
Fe_2O_3	-	-	-	-	-
FeO	5.35	4.88	5.63	4.87	7.49
MgO	5.93	5.90	6.44	5.53	8.89
CaO	12.80	15.17	10.56	17.26	6.84
Na_2O	-	-	-	0.34	0.42
K_2O	3.96	3.38	4.09	3.57	4.02
MnO	-	-	-	0.19	-
P_2O_5	-	-	-	-	-
SO_3	-	-	0.27	-	0.18
	73.16	70.04	76.73	73.11	81.05

Table 6.18: Electron Microprobe Analyses. Microfacies C, 0839

	1	2	3	4	5	6	7	8
SiO_2	0.73	0.21	0.47	0.67	2.76	0.51	9.00	2.87
Al_2O_3	0.44	-	-	0.30	1.33	0.18	3.81	1.25
TiO_2	-	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-	-
FeO	-	-	-	-	0.54	-	1.30	0.41
MgO	0.46	0.43	0.27	0.53	0.74	0.58	1.86	1.01
CaO	52.45	52.05	52.58	51.62	48.83	50.90	39.53	48.19
Na_2O	-	-	-	-	-	-	-	-
K_2O	-	-	-	-	0.39	-	1.15	0.45
MnO	-	0.16	-	-	-	0.21	0.23	0.23
P_2O_5	-	-	-	-	-	-	-	-
SO_3	0.58	1.36	1.24	0.60	0.43	0.57	0.99	0.21
	54.66	54.21	54.56	53.72	55.02	52.95	57.77	54.61

	9	10	11	12	13	14	15	16
SiO_2	6.00	-	-	0.15	0.15	-	2.08	3.18
Al_2O_3	3.14	-	-	-	-	-	0.99	1.29
TiO_2	0.23	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-	-
FeO	0.98	-	-	-	-	-	0.34	0.50
MgO	1.37	0.25	0.30	0.42	0.40	1.15	0.64	0.83
CaO	44.56	53.23	51.56	51.70	51.31	51.91	49.46	49.03
Na_2O	-	-	-	-	-	-	-	-
K_2O	0.80	-	-	-	-	-	0.25	0.34
MnO	0.44	0.36	0.17	0.19	0.24	-	0.26	0.33
P_2O_5	-	0.18	-	-	-	-	-	-
SO_3	0.20	0.34	1.69	1.28	0.51	-	0.20	0.20
	57.72	54.36	53.72	53.74	52.61	52.06	54.21	55.70

Table 6.19: Electron Microprobe Analyses. Microfacies C, 0815.

	1	2	3	4	5	6
SiO_2	-	0.19	0.58	0.32	0.62	0.16
Al_2O_3	-	0.25	0.32	0.15	0.46	0.17
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	-	-	0.14	-	0.20	-
MgO	0.22	0.24	0.34	0.36	0.35	0.20
CaO	57.14	58.33	55.84	58.04	56.59	55.60
Na_2O	-	-	-	-	-	-
K_2O	-	-	-	-	-	-
MnO	0.29	0.14	0.21	-	0.18	0.20
P_2O_5	-	-	-	-	-	-
SO_3	0.46	0.34	0.30	0.23	0.48	0.33
	58.11	59.49	57.73	59.10	58.88	56.66

	7	8	9	10	11	12
SiO_2	-	-	0.15	0.96	0.32	-
Al_2O_3	0.18	-	-	0.42	0.19	-
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	-	-	-	-	-	-
MgO	-	0.31	0.24	0.31	0.22	-
CaO	56.27	56.57	56.49	54.93	57.06	57.90
Na_2O	-	0.31	-	-	-	-
K_2O	-	-	-	-	-	-
MnO	-	-	-	0.21	0.22	0.19
P_2O_5	-	-	-	-	-	-
SO_3	0.18	0.67	0.28	0.33	0.50	0.34
	56.63	57.86	57.16	57.16	58.51	58.43

Table 6.20: Electron Microprobe Analyses. Cross-Analysis of a Calcite Crystal, Microfacies C, 0815

	1	2	3	4	5
SiO_2	0.29	-	0.21	0.19	0.21
AL_2O_3	0.17	0.16	0.16	-	0.29
TiO_2	-	-	-	-	0.14
Fe_2O_3	-	-	-	-	-
FeO	-	-	-	-	-
MgO	0.35	0.25	0.38	0.32	0.30
CaO	55.15	54.79	55.23	55.13	54.47
Na_2O	-	-	-	-	-
K_2O	-	-	-	-	-
MnO	0.17	-	0.16	0.16	0.34
P_2O_5	-	-	-	-	-
SO_3	0.33	5.24	0.39	0.43	0.30
	56.46	60.44	56.53	56.23	56.05

	6	7	8	9
SiO_2	0.17	0.14	0.38	-
Al_2O_3	-	-	-	0.30
TiO_2	-	-	-	-
Fe_2O_3	-	-	-	-
FeO	-	-	-	-
MgO	-	-	0.38	0.28
CaO	55.18	55.68	55.97	55.90
Na_2O	-	-	-	0.29
K_2O	-	-	-	-
MnO	-	0.22	-	0.14
P_2O_5	-	-	-	-
SO_3	0.52	1.12	0.38	1.16
	55.87	57.16	57.11	58.07

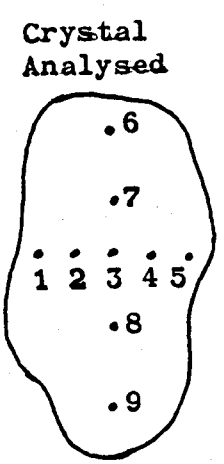


Table 6.21: Electron Microprobe Analyses. Cross-Analysis of a Calcite Crystal, Microfacies C, 089

	1	2	3	4	5
SiO_2	-	-	0.19	-	-
Al_2O_3	-	0.31	-	0.21	-
TiO_2	-	-	-	-	-
Fe_2O_3	-	-	-	-	-
FeO	-	-	-	-	-
MgO	0.35	0.39	0.44	0.41	0.41
CaO	58.07	59.00	57.35	57.21	57.50
Na_2O	-	-	-	-	-
K_2O	0.23	-	-	-	-
MnO	0.29	0.30	-	0.30	0.27
P_2O_5	-	-	-	0.39	-
SO_3	0.62	0.58	0.31	0.40	0.57
	59.56	60.58	58.29	58.92	58.75

Crystal Analysed

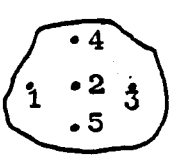


Table 6.22: Electron Microprobe Analyses. Microfacies C, 0815

	1	2	3	4	5	6
SiO_2	3.61	3.22	3.49	2.67	3.74	2.99
Al_2O_3	-	-	-	-	-	-
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	-	-	-	-	-	-
MgO	-	-	-	-	-	-
CaO	0.32	0.45	0.37	0.35	-	0.16
Na_2O	-	-	-	-	-	-
K_2O	-	-	-	-	-	-
MnO	-	-	-	-	-	-
P_2O_5	-	-	-	-	-	-
SO_3	34.71	34.41	34.21	35.21	34.07	35.43
BaO	2.33	0.40	-	0.67	0.93	0.87
	40.97	38.48	38.07	38.90	38.74	39.45

	7	8	9	10	11	12
SiO_2	3.00	4.52	2.56	3.53	2.64	4.04
Al_2O_3	-	-	-	-	-	-
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	-	-	-	-	-	-
MgO	-	-	-	-	-	-
CaO	0.54	0.38	8.24	0.48	1.97	11.34
Na_2O	-	-	-	-	-	-
K_2O	-	-	-	-	-	-
MnO	-	-	-	-	-	-
P_2O_5	-	-	-	-	-	-
SO_3	34.63	34.94	29.67	34.44	30.96	26.10
BaO	0.43	0.53	1.22	0.92	0.60	0.47
	38.60	40.37	41.69	39.37	36.17	42.12

Table 6.23: Electron Microprobe Analyses. Microfacies C, 0815

	1	2	3	4	5
SiO_2	-	0.36	-	0.46	-
Al_2O_3	0.33	0.17	-	-	0.16
TiO_2	-	-	-	0.18	-
Fe_2O_3	-	-	-	-	-
FeO	-	-	-	-	-
MgO	0.24	0.25	-	-	0.26
CaO	54.71	53.88	55.56	52.00	48.51
Na_2O	-	-	-	-	-
K_2O	-	-	-	-	-
MnO	-	-	0.26	-	-
P_2O_5	-	0.22	-	-	-
SO_3	5.78	1.18	2.25	2.79	29.60
	61.06	56.06	57.81	55.43	78.53

Table 6.24: Electron Microprobe Analyses. Microfacies C, 0828

	1	2	3	4	5	6	7	8
SiO_2	0.27	0.48	0.41	0.37	0.57	0.44	0.80	0.26
Al_2O_3	-	0.25	-	-	-	-	0.28	-
TiO_2	-	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-	-
FeO	-	-	-	-	-	-	-	-
MgO	0.54	0.37	0.50	0.57	-	-	-	-
CaO	36.45	19.61	50.42	52.48	-	0.16	-	-
Na_2O	-	-	-	-	0.60	0.45	0.49	0.59
K_2O	-	-	-	-	-	-	-	-
MnO	-	0.24	0.34	0.37	0.27	0.24	-	0.36
P_2O_5	-	-	-	-	-	0.45	-	-
SO_3	16.10	26.70	4.96	4.79	35.04	32.30	34.85	28.60
BaO	12.96	23.52	3.33	2.12	28.87	26.76	28.68	25.02
	69.32	71.17	59.96	60.70	65.35	60.80	65.10	54.83

Table 6.25: Electron Microprobe Analyses. Clay Concentrations in Microfacies C, 085 (A) and 0815 (B)

	1A	2A	3A	4A	1B	2B	3B	4B
SiO_2	48.63	17.66	36.58	4.03	6.62	15.98	6.78	14.22
Al_2O_3	21.76	8.31	16.51	1.95	2.84	6.90	3.28	6.17
TiO_2	0.39	0.24	0.28	-	-	0.28	-	-
Fe_2O_3	-	-	-	-	-	-	-	-
FeO	6.31	2.41	5.68	0.71	0.88	2.53	1.12	2.21
MgO	9.24	4.82	8.38	0.80	1.82	3.31	1.76	15.76
CaO	1.71	37.13	15.74	52.45	48.71	29.32	46.26	20.98
Na_2O	1.36	-	0.74	-	-	-	-	-
K_2O	5.76	1.75	4.03	0.91	0.69	1.63	0.86	1.77
MnO	-	0.15	-	0.19	0.31	0.30	-	0.17
P_2O_5	-	-	-	-	-	-	-	-
SO_3	-	-	-	-	0.16	-	0.33	0.18
	95.16	72.47	87.94	61.04	62.03	60.25	60.39	61.46

Table 6.26: Electron Microprobe Analyses. Ferroan Dolomite Veinlet, 0820

	1	2	3	4	5	6	7
SiO_2	0.26	-	-	-	-	0.25	-
Al_2O_3	-	0.15	0.20	-	0.30	-	-
TiO_2	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-
FeO	2.30	2.54	2.84	3.06	2.81	3.02	2.48
MgO	17.82	18.35	16.86	17.19	16.81	16.94	17.75
CaO	31.29	31.95	32.04	32.20	31.42	32.00	30.46
Na_2O	-	-	-	-	-	-	-
K_2O	-	-	-	-	-	-	-
MnO	0.38	-	0.15	0.24	0.21	0.17	0.43
P_2O_5	-	-	-	-	-	-	-
SO_3	-	-	-	-	-	-	-
	52.05	52.99	52.09	52.69	51.55	52.38	51.12

	8	9	10	11	12	13	14
SiO_2	-	-	-	-	-	-	-
Al_2O_5	-	-	-	-	-	-	-
TiO_2	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-
FeO	2.71	2.79	2.94	2.60	2.94	2.78	2.74
MgO	17.04	17.09	17.44	17.39	16.85	17.14	17.25
CaO	31.77	32.88	31.29	32.00	30.91	31.35	32.11
Na_2O	-	-	-	-	-	-	-
K_2O	-	-	-	-	-	-	-
MnO	-	-	0.21	-	0.27	0.20	-
P_2O_5	-	-	-	-	-	-	-
SO_3	-	-	-	-	-	-	-
	51.52	52.76	51.88	51.99	50.97	51.47	52.10

Table 6.27: Electron Microprobe Analyses. Calcite Veinlet, 08278 (A) and 0828 (B)

	1A	2A	3A	4A	5A	6A
SiO_2	-	0.20	1.83	-	0.24	-
Al_2O_3	-	-	0.79	0.18	0.22	-
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	0.26	0.29	0.60	0.15	0.28	0.19
MgO	0.67	1.13	1.55	0.80	0.42	0.44
CaO	54.28	55.15	54.76	54.30	56.06	55.39
Na_2O	-	-	-	-	-	-
K_2O	-	-	0.18	-	-	-
MnO	1.10	1.05	1.13	1.19	0.73	1.03
P_2O_5	-	-	-	-	-	-
SO_3	0.23	-	-	0.24	0.41	0.55
	56.54	57.82	60.84	56.86	58.36	57.60

	1B	2B	3B	4B	5B	6B
SiO_2	0.19	0.21	-	-	-	-
Al_2O_3	0.39	-	-	-	-	-
TiO_2	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-
FeO	0.20	-	0.28	-	-	-
MgO	1.05	0.67	0.81	0.74	0.75	0.81
CaO	57.13	55.86	55.18	55.09	55.95	55.42
Na_2O	-	-	-	-	-	-
K_2O	-	-	-	-	-	-
MnO	1.08	1.04	0.92	1.08	1.05	0.97
P_2O_5	-	-	-	-	-	-
SO_3	0.47	0.61	0.39	0.57	0.58	0.54
	60.51	58.39	57.58	57.48	58.33	57.74

Table 6.28: Electron Microprobe Analyses of a Veinlet, 089

	1	2	3	4	5
SiO_2	-	0.19	19.67	19.16	20.00
Al_2O_3	0.49	-	3.24	2.99	3.10
TiO_2	-	-	-	0.57	-
Fe_2O_3	-	-	-	-	-
FeO	-	-	-	-	-
MgO	20.50	-	0.90	0.73	0.96
CaO	33.25	56.88	0.18	-	0.23
Na_2O	0.83	-	-	-	0.54
K_2O	0.19	0.12	-	0.13	-
MnO	0.43	0.17	-	-	-
P_2O_5	-	-	-	-	-
SO_3	0.39	0.26	46.62	46.53	46.72
.	56.08	57.62	70.61	70.11	71.55

	6	7	8	9	10
SiO_2	18.93	18.74	20.21	0.21	0.18
Al_2O_3	1.48	1.48	2.94	0.39	0.40
TiO_2	-	0.34	-	-	-
Fe_2O_3	-	-	-	-	-
FeO	-	-	-	-	-
MgO	-	-	0.55	0.65	21.25
CaO	0.25	0.26	0.22	57.15	34.35
Na_2O	-	-	-	-	0.78
K_2O	-	-	-	-	-
MnO	-	-	-	-	0.23
P_2O_5	-	-	-	-	-
SO_3	46.04	46.05	46.05	-	0.41
	66.70	66.87	69.97	58.40	57.60

Table 6.29: Electron Microprobe Analyses. Cavity-Cement, 0842 A

	1	2	3	4	5	6	7	8
SiO_2	0.25	-	-	-	-	-	0.15	-
Al_2O_3	0.28	-	-	-	-	-	-	-
TiO_2	-	-	-	-	-	-	-	-
Fe_2O_3	-	-	-	-	-	-	-	-
FeO	-	-	-	-	-	-	-	-
MgO	0.33	0.23	0.36	-	0.21	0.28	-	0.38
CaO	56.14	57.31	55.57	55.31	57.28	57.24	55.08	56.04
Na_2O	-	-	-	-	-	-	-	-
K_2O	-	-	-	-	-	-	-	-
MnO	-	-	-	-	-	-	-	-
P_2O_5	-	-	-	-	-	-	-	-
SO_3	-	-	-	-	-	-	-	-
	57.00	57.54	55.93	55.31	57.49	57.52	55.23	56.42

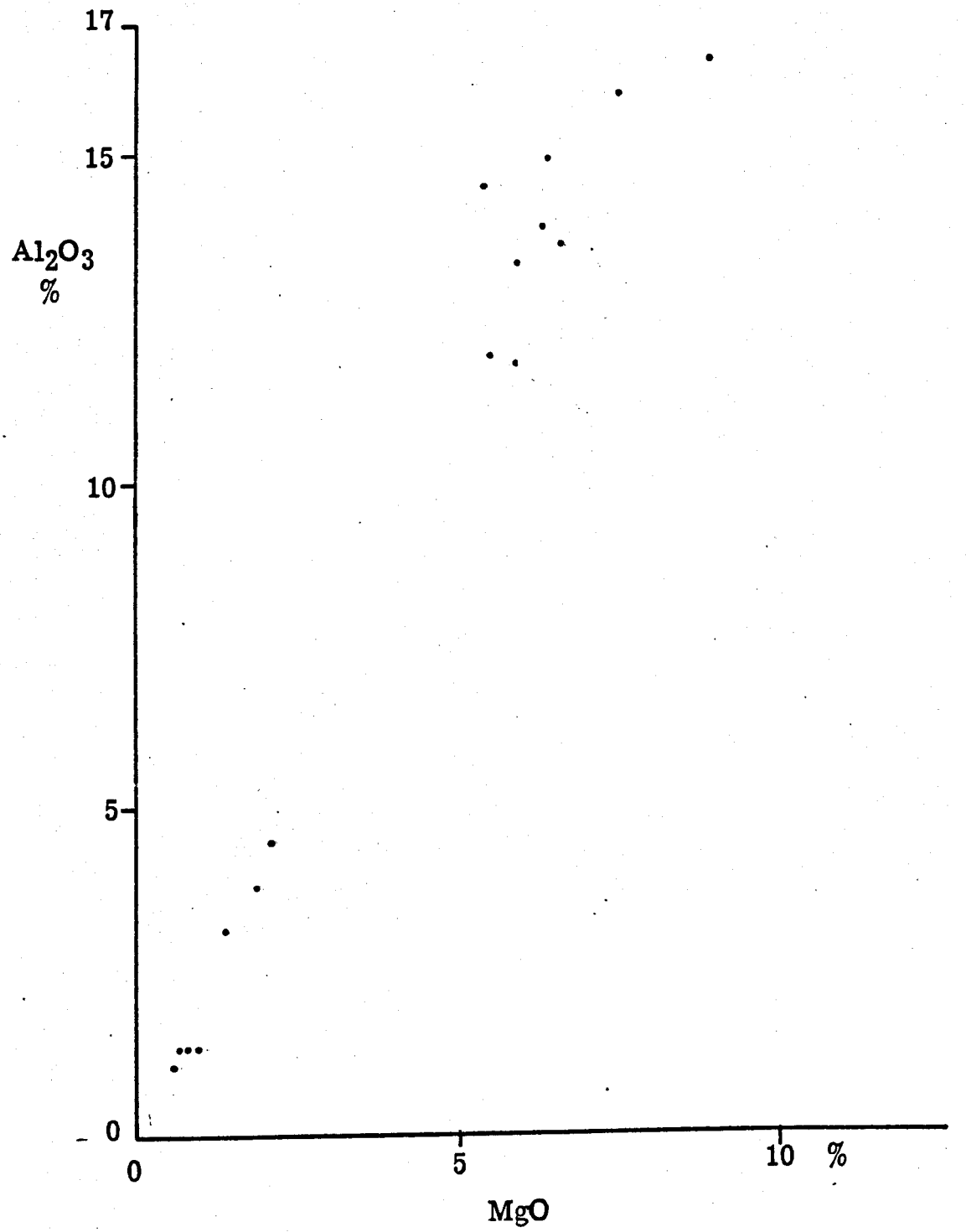


Fig. 6.29 : Plots of Al_2O_3 against MgO of original sediment OB39 (analyses of table 6.17 and analyses 5, 7, 8, 9, 15 and 16 of table 6.18).

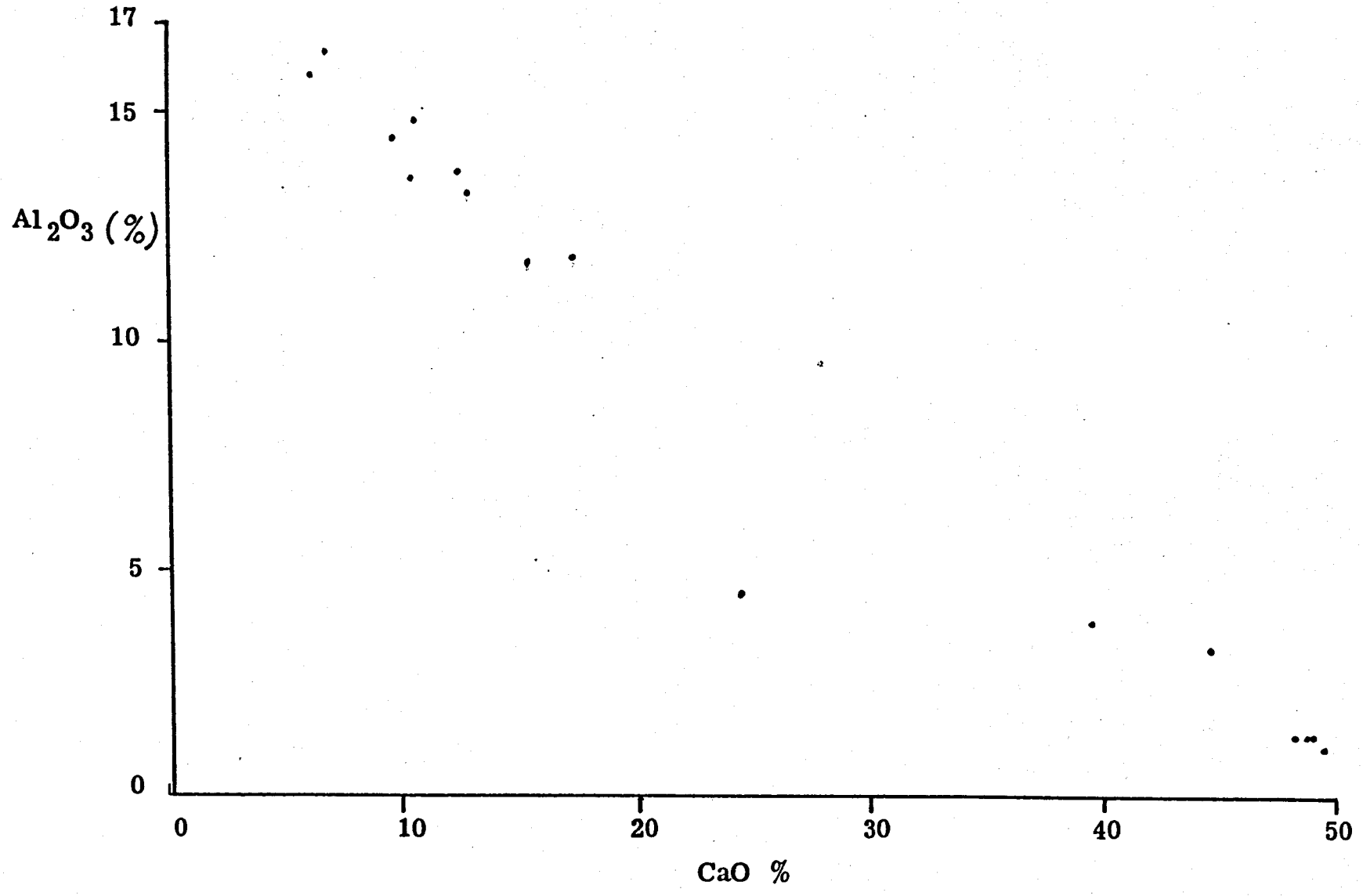


Fig. 6.30 : Plots of Al_2O_3 against CaO in original sediment, OB39. (Analyses in table 14 and analyses 5, 7, 8, 9, 15 and 16 in table 15)

CHAPTER SEVEN

CLASSIFICATION

According to the composition of the carbonates of the Ballagan Formation, which shows that they are mostly dolomites, only dolomite will be briefly discussed in the following section.

Definition of Dolomite

Dolomites are those varieties of carbonate rocks containing more than 50 percent of the mineral dolomite.

During this century, the occurrence and origin of dolomites have been under intensive investigation. This investigation has shown that carbonate rocks, which contain a variable amounts of the mineral dolomite, are most commonly associated with limestones, but also occur with evaporites and terrigenous sediments, both with and without limestones.

Two approaches as to the terminology of dolomite have evolved from the different studies carried out in this field. One of these approaches is purely descriptive, and depends on the proportions of dolomite and calcite in carbonate deposits. The other is based on the inferred origin of dolomite.

The/

The "dolomite question" has remained unsolved by geologists, over a long period of time, simply because neither of these two approaches has brought its solution any nearer. But the development of X-ray diffraction techniques, has caused drastic changes in this stalemate, i.e. in the understanding of dolomite mineralogy and origin. Furthermore, discovery of dolomite forming in recent areas of carbonate sedimentation, has contributed to the reasonable understanding of both origin and occurrence of dolomite in the geologic record (Alderman and Skinner, 1957; Taft, 1961; Bissell and Chilingar, 1962; Wells 1962; Curtis et al, 1963; von der Borch, 1964; Deffeyes et al, 1965; Illing et al, 1965; Shinn et al, 1965; Friedman, 1966, 1980; and Muir et al, 1980).

The literature on the "dolomite question" is enormous and beyond the scope of this study. It has been reviewed by workers including Fairbridge (1957); Friedman and Sanders (1967); and Zenger (1972). The author (Ghummed, 1973) gave a brief summary of the theories on origin of dolomite. Recently Zenger et al (1980) edited a book containing 15 papers, dealing with different aspects of dolomite.

In addition to the investigation of the aspects of the chemical and physical properties and diagenesis of carbonate rocks, some workers had devoted some time to the classification of these rocks in order to facilitate their naming and identification. This objective/

objective, however, has not been achieved to-date, simply because almost every worker has devised a classification scheme that serves his purpose, and consequently, a large number of classification schemes have emerged.

The task of reviewing the literature on the classification of carbonate rocks is beyond the scope of this study, but some of the schemes relevant to this work will be briefly mentioned, otherwise, reference should be made to Ham (1962) where about ten different classification schemes were described and Bissell and Chilingar (1967) who reviewed most of the existing literature concerned. There are two major types of classification widely used, these are identified as descriptive and genetic.

The rocks in question are generally fine in texture and vary in composition between nearly pure dolomite to limestone, but the majority being calcitic dolomite. Therefore, it is felt advisable that the classification schemes based on chemical composition are adopted. Some of these schemes are those of Vishnyakov (1933 in Chilingar, 1960); Teodorovich (1950, in Chilingar, 1960), Chilingar (1957), Dunbar and Rodgers (1957), Pettijohn (1957), Leighton and Pendexter (1962, in Ham, 1962), Bissell and Chilingar (1967) and Friedman and Sanders (1978).

The/

The classification of carbonate rocks on the basis of CaO/MgO ratio was pioneered by Vishnyakov (1933, in Chilingar, 1960), as shown in Table 7.1.

A similar scheme to that of Vishnyakov based on calcite and dolomite contents was proposed by Teodorovich (1935, in Chilingar, 1960), this scheme is illustrated in Table 7.2.

Teodorovich (1958, in Bissell and Chilingar, 1967) recognized several groups of dolomite as given in Table 7.3. Frolova (1959 in Bissell and Chilingar, 1967) published exactly the same classification.

Cayeux (1935, in Bissell and Chilingar, 1967) classified the rocks intermediate in composition between pure limestones and dolomites as given in Table 7.4.

Pettijohn (1948) believed that a classification scheme must be based on parameters which are significant in terms of the origin of the rock under consideration and rejected purely descriptive classifications not based on genesis, which is the ultimate aim of any study of rocks, while Ham and Pray (1962, p.6-7), although admitting the usefulness of genetic classifications, believe that the use of such classification on its own "puts the cart before the horse" for most geologic investigations. They alternatively conclude/

conclude that a classification that will best serve the requirements of geologists can be neither purely descriptive nor purely genetic.

Dunbar and Rodgers (1957) classified carbonate rocks on the basis of composition, dolomitic limestones are those limestones containing more than 10 percent but less than 50 percent dolomite of the combined calcite and dolomite, calcitic dolomite is that dolomite in which calcite is more than 10 percent but less than 50 percent of the combined dolomite and calcite and dolomite is a sedimentary rock containing more than 50 percent of the mineral dolomite.

Pettijohn (1957) defined dolomites as those varieties of limestone containing more than 50 percent carbonate, of which more than half is dolomite. Rocks of intermediate composition between dolomite and limestone were named on the basis of the predominance of calcite over dolomite or vice versa.

Leighton and Pendexter (1962, in Ham, 1962) defined dolomites as carbonate rocks composed of more than 50 percent by weight of the mineral dolomite. They believed that the different types can be accommodated by a descriptive system of nomenclature, one based primarily on compositional grouping and with appropriate modifying textural/

textural terms. They recognised two groups :

1. Calcereous dolomites:- Those containing 50-90% dolomite.
2. Dolomites:- Those containing 90% or more dolomite.

Chilingar (1957, 1967) considered the classification of carbonate rocks on the basis of Ca/Mg ratios to be a very convenient and practical method, Table 7.5.

Friedman and Sanders (1978) proposed a genetic classification for dolomites as follows :-

1. Syngenetic dolomite:- Dolomite that has formed penecontemporaneously in the environment of deposition.
2. Diagenetic dolomite:- Dolomite formed by replacement of calcium carbonate sediments or limestone during or following consolidation such as within beds of carbonate sediments or limestone.
3. Epigenetic dolomite:- Dolomite that has formed by localized replacement of limestone along post depositional structural elements such as faults and fractures.

The carbonates of the Ballagan Formation are found to be mainly dolomites on the basis of chemical composition. The application of any compositional classification scheme mentioned above shows that at least 86 percent of these carbonates fall in the dolomite region with variable calcite proportions (Tables 7.6-10). According to Frolova and Vishnyakov schemes, nearly 61 percent of them are found/

found to be only slightly calcareous dolomites, while Teodorovich classification shows that only 23 percent are slightly calcareous dolomites (Tables 7.7 and 7.6 respectively). The other 14 percent of the carbonates are limestones, similarly with different dolomite contents. Only between 1 and 6 percent are found to be slightly dolomitic limestones to limestones.

Considering the groupings of the carbonates together with their other characteristics mentioned elsewhere, a syngenetic origin in terms of Friedman and Sanders classification is believed highly probable, namely,the majority, if not all, of carbonates were most likely deposited as chemically precipitated dolomitic muds.

Table 7.1 Vishnyakov's (1933) Classification of Limestones and Dolomites

Type	$CaCO_3$ Content, %	$CaMg(CO_3)_2$ Content, %	CaO/MgO ratio
Limestone	95-100	5 - 0	50.1 - ~
Slightly dolomitic limestone	75- 95	25 - 5	9.1 - 50.1
Dolomitic limestone	50-75	50 - 25	4.0 - 9.1
Calcitic dolomite	25-50	75 - 50	2.2 - 4.0
Slightly calcitic dolomite	5-25	95 - 75	1.5 - 2.2
Dolomite	0-5	100 - 95	1.4 - 1.5

Table 7.2/

Table 7.2: Teodorovich's (1935) Classification of Calcite-Dolomite Series

Type	Calcite Content %	Dolomite Content %
Limestone	100 - 95	0 - 5
Slightly dolomitic limestone	95 - 80	5 - 20
Medium dolomitic limestone	80 - 65	20 - 35
Highly dolomitic limestone	65 - 50	35 - 50
Highly calcitic dolomite	50 - 35	50 - 65
Medium calcitic dolomite	35 - 20	65 - 80
Slightly calcitic dolomite	20 - 5	80 - 95
Dolomite	5 - 0	95 - 100

Table 7.3: Teodorovich's (1958) Classification of Dolomites

Group Name	Content %		
	Dolomite	Calcite	Clayey material
Clayey dolomite	35 - 90	0 - 45	30 - 10
Slightly clayey calcitic dol.	90 - 45	5 - 47.5	5 - 10
Slightly clayey dolomite	95 - 85	0 - 5	5 - 10
Dolomite	100 - 90	0 - 5	0 - 5
Slightly calcitic dolomite	95 - 80	5 - 20	0 - 5
Calcitic dolomite	80 - 65	15 - 35	0 - 5
Highly calcitic dolomite	65 - 47.5	30 - 50	0 - 5

Table 7.4: Classification of rocks intermediate in composition between pure limestones and dolomites (After data by Cayeux, 1935; Carozzi, 1960, p.264)

Rock Name	Content %	
	Calcite	Dolomite
Limestone	> 95	< 5
Magnesian Limestone	90 - 95	5 - 10
Dolomitic Limestone	50 - 90	10 - 50
Calcitic dolomite	10 - 50	50 - 90
Dolomite	< 10	> 90

Table 7.5 : Chilingar's (1967) classification of limestones and dolomites on basis of Ca/Mg ratio

Name	Range in Ca/Mg Ratio
Magnesian dolomite	1.0 - 1.5
Dolomite	1.5 - 1.7
Slightly calcareous dolomite	1.7 - 2.0
Calcareous dolomite	2.0 - 4.74
Highly dolomitic limestone	4.74- 16.0
Dolomitic limestone	16.0 - 60.0
Slightly dolomitic (or magnesian limestone)	60.0 -105.0
Calcitic limestone	> 105.0

Note : All Ca/Mg ratios presented here are weight ratios

Table 7.6 : Classification of Carbonate Beds, Ballagan Formation, using Teodorovich's (1935) Classification

Type (dolomite content %)	Loch Thom	Ben Bowie	Auchenreoch Glen	Overtoun Burn	Ballagan Glen	Little Corrie	Gargunnock Burn	Total
Dolomite (100 - 95%)	-	-	-	-	-	-	-	-
Sl. calcitic dolomite (95 - 80%)	-	-	60	14	30	9	15	128 24%
Med. calcitic dolomite (80 - 65%)	12	27	53	26	61	96	55	330 61%
Highly calcitic dol. (65 - 50%)	5	-	1	1	1	2	3	13 2%
Highly dol'tic limest. (50 - 35%)	-	-	-	1	14	10	3	28 5%
Med. dol'tic limest. (35 - 20%)	-	-	6	4	-	7	1	18 3%
Slightly dol'tic limest. (20 - 5%)	3	3	2	6	-	8	1	23 4%
Limestone (5 - 0%)	-	1	2	-	-	-	-	3 1%
	20	31	124	52	106	132	78	543

Sl = slightly, Med. = medium, Dol'tic = dolomitic, Limest.= Limestone, Dol. = Dolomite.

Table 7.7: Classification of Carbonate Beds, Ballagan Formation using Vishnyakov (1933, 1950) and Frolova (1959) classifications

Type (CaO/MgO ratio)	Loch Thom	Ben Bowie	Auchenreoch Glen	Overtoun Burn	Ballagan Glen	Little Corrie	Gargunnock Burn	Total
Dolomite (1.4 - 1.5)	-	-	-	-	-	-	-	-
Sl.calcitic dolomite (1.5 - 2.2)	9	18	102	38	72	43	48	330 61%
Calcitic dolomite (2.2 - 4.0)	8	9	11	2	20	64	25	139 26%
Dolomitic limestone (4.0 - 9,1)	-	-	1	4	14	16	4	39 7%
Sl. dol'tic limestone (9.1 - 50.1)	3	-	8	7	-	9	1	28 5%
Limestone 50.1	-	4	2	1	-	-	-	7 1%
	20	31	124	52	106	132	78	543

Table 7.8 : Classification of Carbonate Beds, Ballagan Formation, using Vishnyakov (1933, 1950) and Frolova (1959) Classifications

Type (dolomite content %)	Loch Thom	Ben Bowie	Auchenreoch Glen	Overtoun Burn	Ballagan Glen	Little Corrie	Gargunnock Burn	Total
Dolomite (100 - 95%)	-	-	-	-	-	-	-	-
Sl.calcitic dolomite (95 - 75%)	9	17	103	39	72	42	48	330 61%
Calcitic dolomite (75 - 50%)	8	10	11	2	20	65	25	141 26%
Dolomitic limestone (50 - 25%)	-	-	1	2	14	16	4	37 7%
Sl. dol'tic limestone (25 - 5%)	3	3	7	9	-	9	1	32 5%
Limestone (5 - 0%)	-	1	2	-	-	-	-	3 1%
	20	31	124	52	106	132	78	543

Table 7.9 : Distribution of carbonate beds using Cayeux (1935) and Carrozi (1960) Classifications

Rock Name (dolomite content %)	Loch Thom	Ben Bowie	Auchenreoch Glen	Overtoun Burn	Ballagan Glen	Little Corrie	Gargunnock Burn	Total
Dolomite	–	–	–	–	–	–	–	–
(90%)	–	–	–	–	–	–	–	–
Calcitic dolomite (90 – 50%)	17	27	114	41	92	107	73	471 86%
Dolomitic limestone (50 – 10%)	2	3	8	9	14	25	5	66 12%
Magnesian Limestone (10 – 5%)	1	–	–	2	–	–	–	3 1%
Limestone (5%)	–	1	2	–	–	–	–	3 1%
	20	31	124	52	106	132	78	543

Table 7.10 : Distribution of carbonate beds using Chilingar's (1957) classification

Type (Ca/Mg ratio)	Loch Thom	Ben Bowie	Auchenreoch Glen	Overtoun Burn	Ballagan Glen	Little Corrie	Gargunnock Burn	Total
Dolomite (1.5 - 1.7)	-	-	-	-	-	-	-	-
Sl. calc. dolomite (1.7 - 2.0)	-	-	-	-	-	-	-	-
Calc. dolomite (2.0 - 4.74)	17	27	114	41	92	107	73	471 86%
Hi. dol'tic limestone (4.74 - 16.0)	-	2	8	7	14	17	4	52 10%
Dol'tic limestone (16 - 60)	3	1	-	3	-	8	1	16 3%
Sl. do'tic limestone (60 - 105)	-	1	2	1	-	-	-	4 1%
	20	31	124	52	106	132	78	543

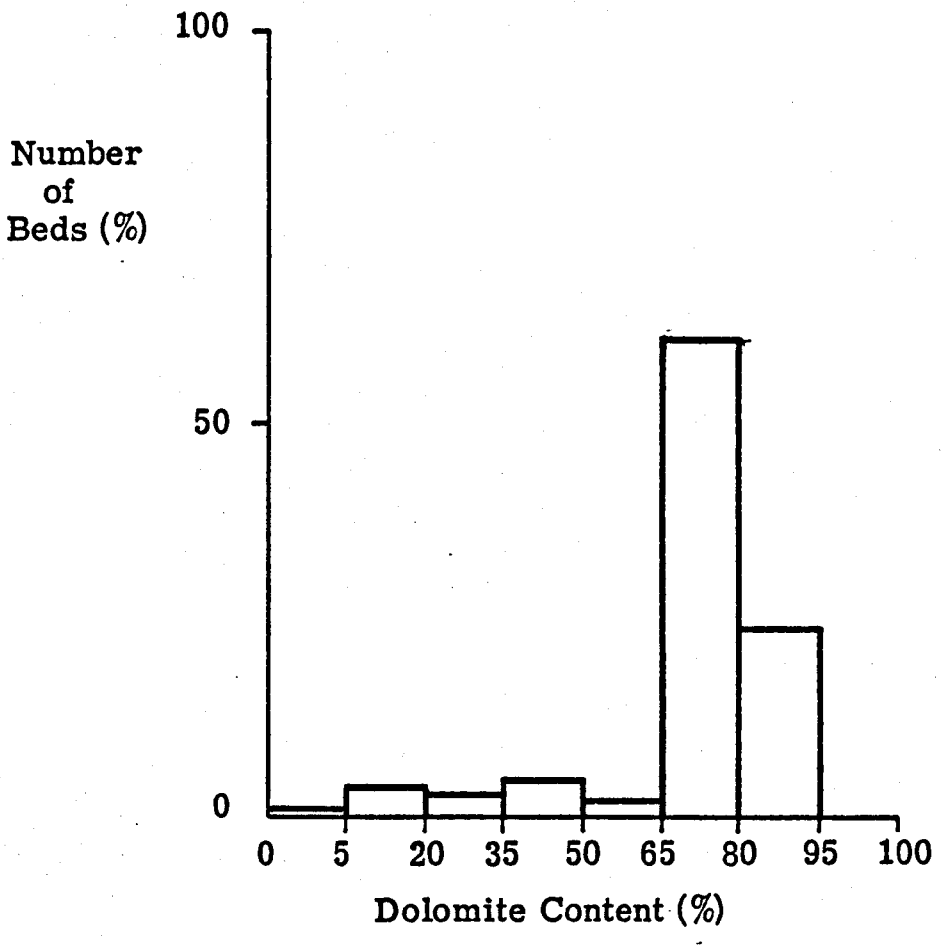


Fig. 7.1 : The distribution of carbonate beds using Teodorvich's (1935) classification

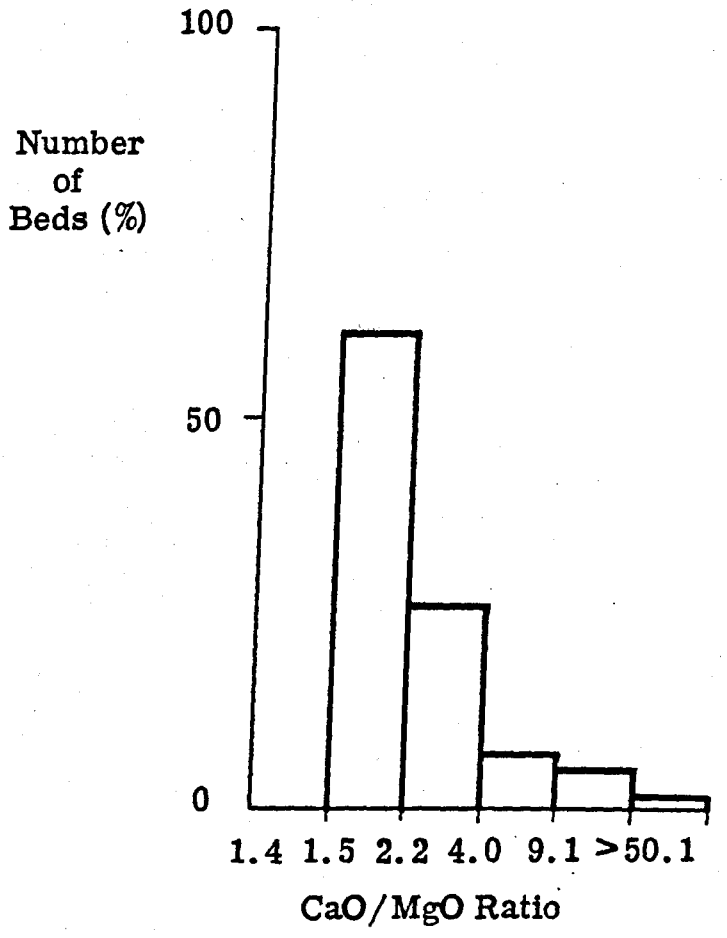


Fig. 7.2 : The distribution of carbonate beds using Vishnyakov's (1933, 1950) and Frolova's (1959) classifications.

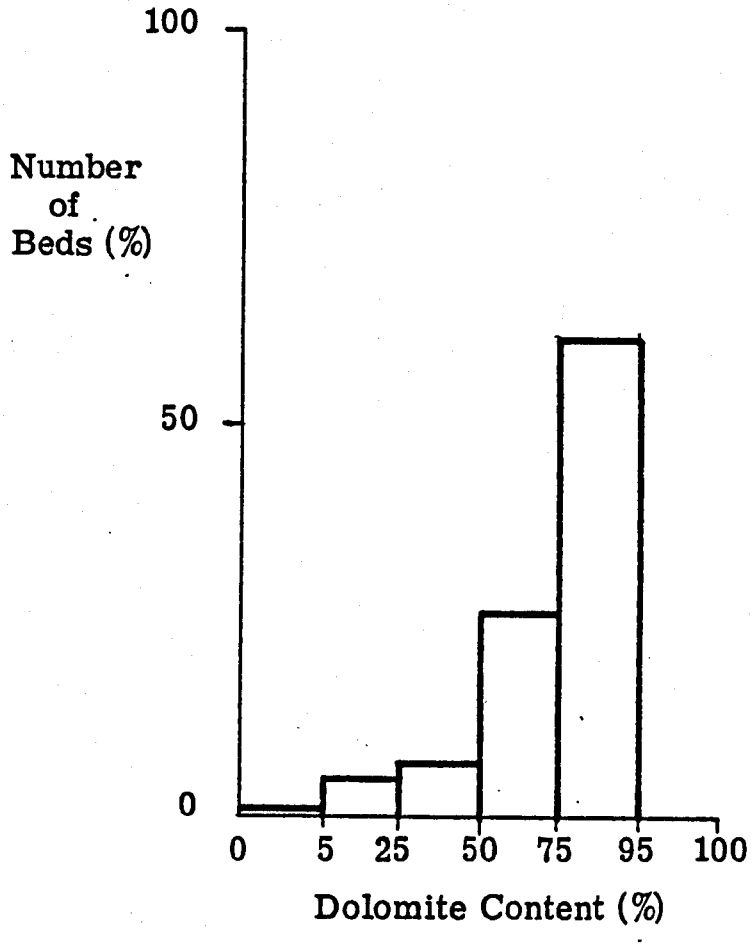


Fig. 7.3 : The distribution of carbonate beds using Vishnyakov's (1933, 1950) and Fralova (1959) classifications.

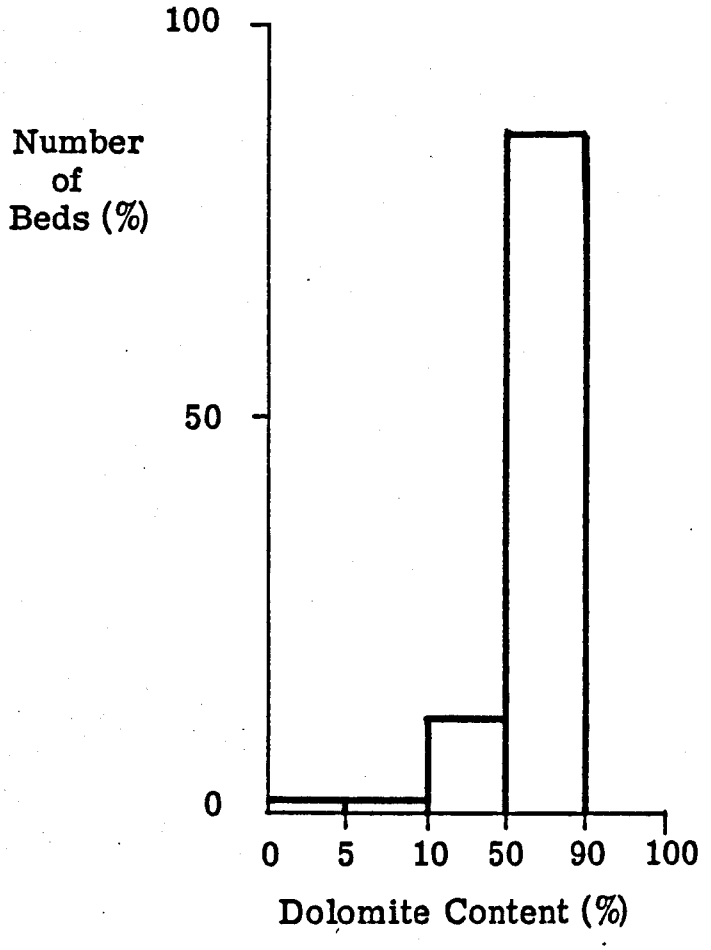


Fig. 7.4 : The distribution of carbonatebeds using Cayeux (1935) and Carrozi (1960) classifications.

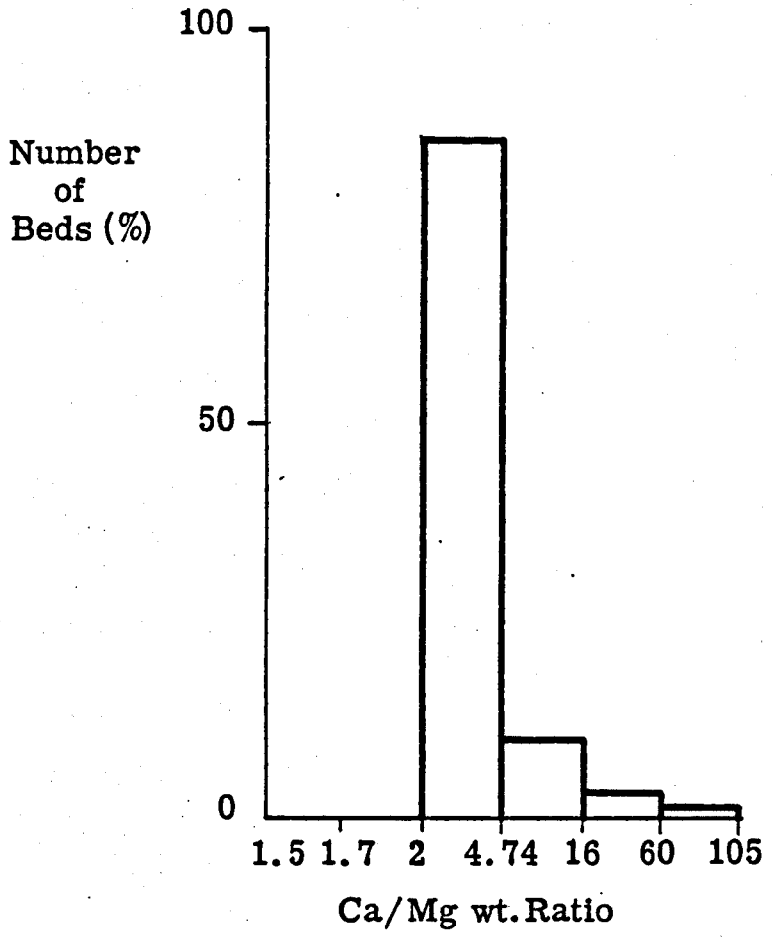


Fig. 7.5 : The distribution of carbonate beds using Chilingar's (1957) classification.

CHAPTER EIGHT

ENVIRONMENTS OF DEPOSITION

The Ballagan Formation represents the lower-most deposits of the Lower Carboniferous, which have accumulated in the Midland Valley, exclusively on a floor of Upper Old Red Sandstone (Freshney, 1961). A palaegeographic map of central and southern Scotland of which the study area is a part, in Visean time is shown in Fig. 8.1 (after George, 1960, Fig. 15, p. 78). A proposed model of depositional environment is shown in Fig. 8.2.

8.1 Main Facts about the Ballagan Formation

The carbonate beds of the Ballagan Formation contain a record of a restricted evaporitic environment of deposition, whereas the lutites indicate that they were accumulated in a more open marine conditions. Any explanation of the Ballagan Formation must take account of the following salient facts:

1 - The formation consists mainly of an alternation of carbonate and lutite.

2 - The carbonates are unfossiliferous (except for probably algae), whereas some lutites contain a marine fauna.

3 - The presence of gypsum and salt (halite) pseudomorphs.

4 - An abundance of shrinkage cracks.

5 - Presence of quartz arenites which are well sorted sandstones.

6 - Transition both downward (into Old Red Sandstone) and laterally (into N. Ayrshire) to red alluvial deposits with caliche./

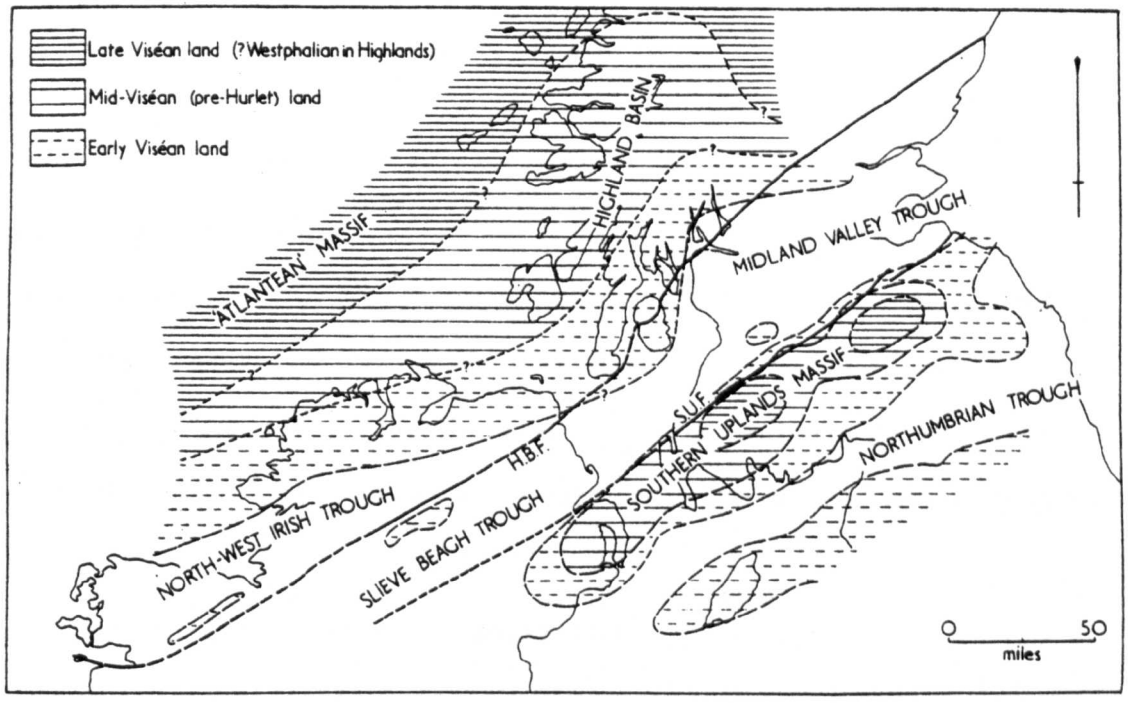


Fig. 8.1 : Palaeogeographic map of Central and Southern Scotland in Visean times.

(from George, 1960; Fig. 15, p78)

caliche.

7 - The carbonates are aphanitic.

8 - The carbonates are thinly bedded.

Some of these features are indicative of the persistence of evaporitic conditions during the time of formation of the carbonate beds. Similar features were used by West et al. (1968) as indicators of the environment of deposition for similar sediments. Lucia (1972) used some of these features as criteria for the recognition of evapotite-carbonate shoreline-sedimentation.

8.2 General Environment of Deposition

The presence of evaporites and the abundance of desiccation cracks indicate generally arid conditions in which water masses were subject to evaporation. This deduction is supported by the transition (downward and laterally) into facies where caliche is found. Caliche is known only to form in arid-semi-arid conditions.

Faunas being found only in shales suggest two things: either they were present in the carbonates but have been destroyed by dolomitization, or they were only present originally in the shales. Since the evaporites are commonly found associated with dolomites, it is likely that no fauna was present at the time of carbonate precipitation. If this is the case, then the marine incursions, bringing new marine waters into this environment, must have been accompanied by muddy water to deposit shale.

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The rapid alternation of lutite and carbonate clearly indicates a periodic or episodic influx of water which was then isolated from the main supply and evaporated out. This process suggests that the sea, from where the incursions were mainly derived, was periodically cut-off from the land, i.e. there was a sea-ward barrier and a partly land-locked lagoon system. The well sorted, quartz-arenitic sandstones are sometimes seen to carry a fish fauna of scales and teeth.

The general environment is, therefore, seen as a lagoon bordered to the landward (in N. Ayrshire) by alluvial deposits and, possibly to the east and further south by more open marine conditions. The lagoons originated by the flooding of the Old Red Sandstone landmass. In this interpretation, the Old Red Sandstone facies is thought to be diachronous: the Ballagan Formation is equivalent to the N. Ayrshire alluvial facies.

The palaeogeography is clearly more complex than suggested by Fig. 8.1. The N. Ayrshire land deposits appear as an elongate ridge bounded by the Ballagan lagoons to the North and the more open marine conditions (represented by the fossiliferous marine beds described by Freshney, 1961, p. 35) to the South.

8.3 The Origin of the Carbonate Beds

From discussions of petrography and microfacies (Chapter Three) it is clear that these beds were initially very fine-grained carbonate (mainly dolomitic) deposits. Fine-grained carbonates of this kind are now known to occur in only a few places./

places. Recent dolomite is found forming in the Coorong region, southeast of South Australia (Alderman and Skinner, 1957; von der Borch, 1976; von der Borch et al., 1964; von der Borch and Lock, 1979; and Muir et al., 1980). The precipitation of dolomite is taking place in a number of ephemeral saline lakes and in a shallow inlet of the sea. The origin of these dolomitic sediments is ascribed to elevated pH caused by plant growth in the lakes. The characteristics of the sediment produced here are similar to those of the carbonate beds in the Ballagan Formation. Another possible area of fine-grained carbonate accumulation were described in 1946 by Teodorovich (in Friedman and Sanders, 1967) who reported the formation of dolomite in Recent sediments, from Alakul Bay in the Eastern part of Lake Balkhash, U.S.S.R. He records increased water temperature; salinity; magnesium content and pH in areas of dolomite formation.

Dolomite sediments are described from many other areas of Recent carbonate deposition, where they are found forming in several different depositional environments: tidal flats (mainly the supratidal zones); sabkhas; and restricted water bodies (lagoons and lakes). These environments occur in the Arabian Gulf (Wells, 1962; Curtis et al., 1963; Shearman, 1963; and Illing et al., 1965); the Red Sea (Friedman, 1966, 1980); Laguna Madre, Texas (Rusnak, 1960); the southern coast of Florida (Taft, 1961); the Salt Flats of Western Utah (Bissell and Chilingar, 1962); Bonaire, Netherlands Antilles (Deffeyes et al., 1965); and Andros Island, Bahamas (Shinn et al., 1965). Dolomites in all these areas are believed to be of penecontemporaneous /

penecontemporaneous if not secondary origin, but some of the workers did not rule out the possibility of their direct precipitation out of hypersaline solutions. The rock and faunal associations from these environments bear some resemblance to those of the Ballagan Formation. However, the Coorong supplies a closer analogy with the strata of the Ballagan Formation.

The dolomitic carbonate minerals in microfacies A of the present study, represent sediments which probably formed as primary precipitates. They crystallized and accumulated in lagoons, locked or possibly semi-locked. The waters in these lagoons were of high salinity, most probably hypersaline, as indicated by both the occurrence of evaporite minerals and lack in fossils. As a result of evaporation both Mg/Ca ratio and pH, two factors essential for dolomite formation, had increased considerably and dolomite formed.

The possibility that some modern and ancient dolomites may have formed as primary chemical precipitates, still a controversial issue with carbonate sedimentologists. Even the intensive studies of Recent carbonate sediments, with the help of X-ray and stable isotope (carbon and oxygen) analysis, seem to have failed to satisfy many scientists with regard to the existence of primary dolomites. However, some workers like Cooper (1956, in Friedman and Sanders, 1967) who examined ancient fine-grained dolomites, support the idea of the primary origin of dolomite.

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The role of clay minerals in the system, with respect of dolomite formation, is unknown. However, Kahle (1965) suggests that the presence of clay minerals may play an important role in the form of ion exchange; nucleation; and crystal growth processes.

The dolomite-calcite proportion in the present study is likely to have been controlled by the properties of the precipitating solution, such as salinity; Mg/Ca ratio; temperature; and pH. The virtual absence of the mineral dolomite from the pseudobrecciated beds, and the presence of calcite in them in significant amounts, may indicate deep conditions, where hypersalinity is less likely to occur.

Poorly preserved laminations are uncommon in the rock section, but are common in thin section. There is no evidence as to their algal origin, but they do, in morphology, resemble algal structures, which are reported of wide spread occurrence in the areas of Recent carbonate sedimentation. These laminations may be also of algal origin on the basis that algal laminations are found in the carbonate sediments of the Coorong region (Muir et al., 1980), where they are also poorly preserved. In both the Ballagan Formation and in the Coorong, the poor preservation may be due to neomorphism.

8.4 A Model for the Origin of Ballagan Formation

The Ballagan Formation consists of an alternation of clastic and carbonate sediments. The sedimentary cycle began by the flooding /

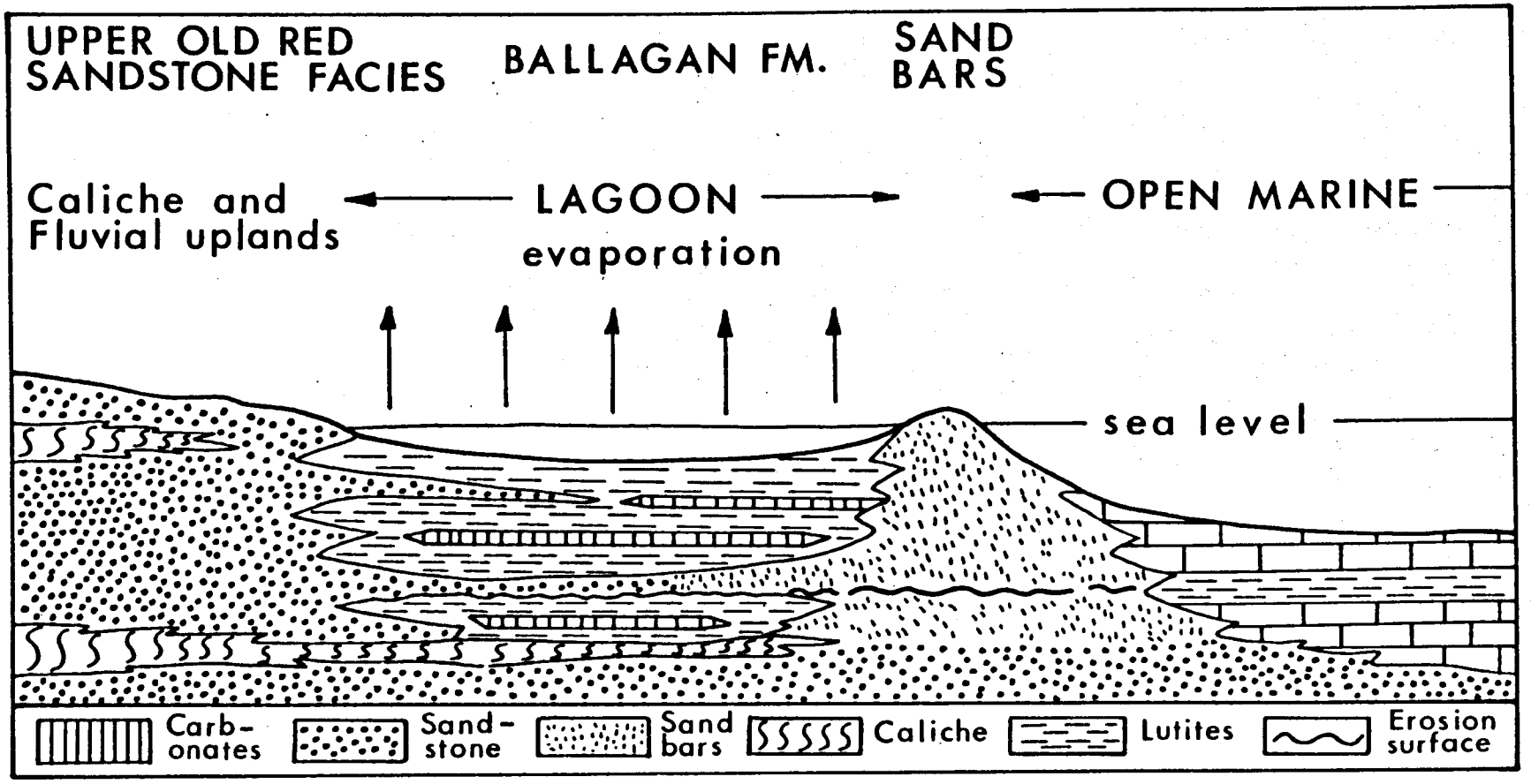

Fig. 8.2: A sketch for the proposed environment of deposition of the Ballagan Formation deposits. Not to scale.

flooding of the Old Red Sandstone landmass, which resulted in the accumulation of the first clastic unit. The area was gradually cut-off from the sea by sedimentation, and a locked lagoon was formed. As a result of the reduction in supply of terrigenous detritus coupled with a climate favouring evaporation, the restricted water body produced carbonate (mainly dolomitic) deposits. The Coorong region (Muir et al., 1980) is a Recent site with a similar cycle of sedimentation. The cycle begins also with a restricted marine unit deposited under a permanent water body. This unit grades upwards into a surficial dolomite which continues to form today in alkaline, ephemeral lakes, which became separated from the restricted marine or lagoonal environment by sedimentation.

The Ballagan Formation deposits were formed under arid conditions as indicated by the presence of evaporite minerals; desiccation cracks; and their transition downward and laterally into facies with caliche, which is known to form only in arid or semi-arid climate. The Coorong region is situated in what seasonally is a relatively humid climate and minor evaporite minerals are precipitated during dry summer months, but are dissolved by water and flushed through lake sediments (Muir et al., 1980).

The characteristics of the Recent dolomite of the Coorong region are similar to those of the dolomites of the present study. Both dolomites are originally aphanitic, their bed-thickness is similar, and are generally unfossiliferous with the exception of the algal material found in both regions. The repeated

development /

development of these algal mats across lake surfaces allows them to be incorporated into the sediment sequence as microlaminations (Muir et al., 1980). The poorly preserved laminations and the brecciated material found in the Ballagan Formation are believed to be of the same origin.

Desiccation cracks which have been generally interpreted as indicators of subaerial exposure, were developed in the Ballagan Formation sediments. They also are of wide spread occurrence in the Coorong region sediments, and both being of similar nature, their origin is, therefore, most likely to be also similar.

Therefore, the petrographical; the structural (desiccation cracks); the faunal (poorly preserved algae); and palaeogeographical evidences all point to the Coorong region as a good model for the Ballagan Formation. The Ballagan Formation differs in that (i) it contains more mud which indicates a source near a river mouth where there is a major influx of sediment into the sea, and (ii) it may have accumulated in a somewhat drier climate regime.

CONCLUSIONS

1. The Ballagan Formation deposits comprise carbonates; lutites and sandstone, they are Upper Tournaisian and possibly Lower Visean in age. They were laid down on a substrate of Upper Old Red Sandstone sediments.

2. The Ballagan Formation sediments were accumulated in a lagoonal environment which was open to the sea periodically.

3. The dolomites were formed as primary chemical precipitates during periods of intense evaporation, when the lagoonal waters were hypersaline and both Mg/Ca ratio and pH were high. Their characteristics resemble those of the Coorong region in South Australia, which is their closest Recent analogue.

4. The dolomite precipitates were sometimes subaerially exposed and shrinkage cracks formed. Some cracks were also formed under a sediment cover in both stratified and nodular carbonate beds.

5. The terrigenous material contained in the carbonate beds is predominantly of wind-blown origin.

6. The carbonate nodules are of syngenetic origin, they were formed by segregation of carbonate minerals while the lutitic sediments were still unconsolidated.

7. Rivers crossed the area where the Ballagan Formation deposits accumulated, they carried sands to the sea. These sands were redistributed and washed back to form offshore sand bars, which isolated the lagoon from the sea. Some fluvial sands also accumulated in this lagoon and culminated in the deposition of the fluvial Spout of Ballagan Sandstone.

8. Diagenetic processes were active in the form of neomorphism; metasomatism; and segregation:

   A - Neomorphism transformed part of the dolomites into a coarser fabric compared to that of the original sediment.

   B - Metasomatism - calcitization of some dolomites occurred in some beds resulting in a coarse fabric of chicken-wire texture, composed almost exclusively of calcite.

   C - Segregation of calcite in argillaceous carbonate beds took place and resulted in the development of a fabric similar to that of B above in every aspect.

9. The carbonates are divided into three microfacies on the basis of crystal-size. They are:

   I. Microfacies A - crystals are less than 5 microns in diameter.

   II. Microfacies B - crystals are usually 5-15 microns in diameter.

   III. Microfacies C - crystals are usually 50-150 microns in their longest diameter.

10. The carbonate beds contain variable amounts of terrigenous material, composed predominantly of clay minerals, mainly illite, and montmorillonite and chlorite are common, and less abundant quartz sand.

11. On the basis of chemical composition, 86% of the carbonate beds are dolomites, they contain more than 50% of the mineral dolomite. Calcite is the second carbonate mineral in abundance, gypsum is of rare occurrence as original sediment.

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